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INORGANIC HALOGEN OXIDIZER RESEARCH

Karl O. Christe, et al

Rocketdyne

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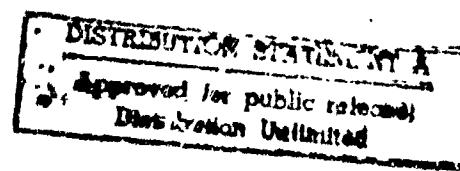
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15. ABSTRACT

Synthesis of novel  $\text{ClF}_3\text{O}_2$  was scaled up and its physical properties were determined. Force constants and thermodynamic properties were computed. Its complex formation with strong Lewis acids was studied and two new salts,  $\text{ClF}_2\text{O}_2^+\text{BF}_4^-$  and  $\text{ClF}_2\text{O}_2^+\text{AsF}_6^-$ , were synthesized.

The  $\text{ClF}_5-\text{OF}_2$  photolysis yielded no  $\text{ClF}_5\text{O}$  and the  $\text{BrF}_5-\text{OF}_2$  system produced no  $\text{BrF}_3\text{O}$  or  $\text{BrF}_5\text{O}$ . Reaction parameters for the synthesis of  $\text{ClF}$  from  $\text{Cl}_2$  and  $\text{ClF}_3$  were determined.

Reactions of  $\text{PtF}_6^-$  with  $\text{OF}_2$ ,  $\text{C}_3\text{F}_8$ ,  $\text{BrF}_5$ ,  $\text{ClF}_3\text{O}$ ,  $\text{C}_2^+\text{ClF}_4\text{O}^-$ ,  $\text{OF}_3\text{NO}$ , were studied. Synthesis of  $(\text{CF}_3)_2\text{NO}^+$  was studied by using  $\text{O}_2^+\text{AsF}_6^-$  as the oxidizing agent on  $(\text{CF}_3)_2\text{NO}$ .

A systematic study of low-temperature ozonization reactions was performed involving  $\text{ClOClO}_3$ ,  $\text{BrOClO}_3$ ,  $\text{ClO}_2$ ,  $\text{BrOSO}_2\text{F}$ ,  $\text{ClONO}_2$ , and  $\text{ClOSO}_2\text{F}$ .

From  $\text{C}_6\text{F}_5\text{I}$  or  $\text{C}_6\text{F}_5\text{Br}$  and  $\text{ClOClO}_3$ , novel compounds,  $\text{C}_6\text{F}_5(\text{OClO}_3)_2$  and  $(\text{O}_3\text{ClO})_2\text{C}_6\text{F}_5\text{Cl}$ , were obtained.

Efforts were made to synthesize  $\text{Br}_2\text{O}_7$  and  $\text{I}_2\text{O}_7$  by reaction of perhalate salts with  $\text{SO}_3$ . For the  $\text{BrO}_4^-$  and  $\text{IO}_4^-$  salts the isolation of  $\text{Br}_2\text{O}_7$  and  $\text{I}_2\text{O}_7$  was not possible owing to complexing with the starting materials.

Covalent fluorosulfates are useful for chemical syntheses and a number of reaction systems were studied involving iodine, sulfur, and selenium fluorides.

A novel synthesis of  $\text{NF}_4^+$  salts was discovered employing uv photolysis. The  $\text{PtF}_6^-$ ,  $\text{AsF}_6^-$ , and  $\text{BF}_4^-$  salts were prepared in this way. This study suggests that  $\text{F}_2$  in the presence of a strong Lewis acid has an oxidizing power comparable to that of  $\text{PtF}_6^-$ .

A number of structural studies were conducted. Among the compounds studied were  $\text{ClF}_4^+$ ,  $\text{BrF}_4^+$ ,  $\text{IF}_4^+$ , and  $\text{SF}_5\text{O}^-$  salts, trifluoroacetates of iodine,  $\text{SF}_4$ ,  $\text{SF}_4\text{O}$ , and  $\text{Cl}_2\text{O}_6$ .

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PREPARED BY

K.O. Christe, C.J. Schack,  
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## FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 429, with Dr. Ralph Roberts as Scientific Officer. This report covers the period 1 April 1972 through 31 March 1973. The program has been directed by Dr. D. Pilipovich, Manager, Exploratory Chemistry. Staff members responsible for the scientific effort were Dr. K. O. Christe, Dr. C. J. Schack, Mr. R. D. Wilson, and Dr. E. C. Curtis. The Program Manager was Dr. B. Tuffly.

## ABSTRACT

The synthesis of the novel heptavalent chlorine oxyfluoride,  $\text{ClF}_3\text{O}_2$ , was scaled up and its physical properties were determined. Its structure was established by  $^{19}\text{F}$  nmr and vibrational spectroscopy and both force constants and thermodynamic properties were computed. Its complex formation with strong Lewis acids was studied and two new salts,  $\text{ClF}_2\text{O}_2^+\text{BF}_4^-$  and  $\text{ClF}_2\text{O}_2^+\text{AsF}_6^-$ , were synthesized. With Lewis bases, such as  $\text{CsF}$ ,  $\text{FNO}$ , or  $\text{FNO}_2$ ,  $\text{ClF}_3\text{O}_2$  does not form adducts. The structure of the  $\text{ClF}_2\text{O}_2^+$  cation was determined by nmr and vibrational spectroscopy and a force field was computed.

A thorough study of the  $\text{ClF}_5\text{-OF}_2$  photolysis yielded no evidence at all of the existence of  $\text{ClF}_5\text{O}$ . It appears that the claim by Zuechner and Glemser for its formation is invalid. Photolysis of the  $\text{BrF}_5\text{-OF}_2$  system did not produce any evidence of new compounds such as  $\text{BrF}_3\text{O}$  or  $\text{BrF}_5\text{O}$ . The interaction between  $\text{ClF}_3\text{O}$  and  $\text{SF}_4$  in the presence of  $\text{CsF}$  did not yield  $\text{FCIO}_2$ , but all the secondary reaction products expected for its disproportionation to  $\text{FCIO}_2$  and  $\text{ClF}$ . Reaction parameters for the synthesis of  $\text{ClF}$  from  $\text{Cl}_2$  and  $\text{ClF}_3$  were determined.

We have continued to study the reaction chemistry of  $\text{PtF}_6$ . Its reactions with  $\text{OF}_2$ ,  $\text{O}_3$ ,  $\text{BrF}_5$ ,  $\text{ClF}_3\text{O}$ ,  $\text{Cs}^+\text{ClF}_4\text{O}^-$ ,  $\text{CF}_3\text{NO}$ , and  $(\text{CF}_3)_2\text{NC}$  were investigated in an attempt to synthesize the novel species,  $\text{OF}_3^+\text{O}_3^-$ ,  $\text{BrF}_6^+$ ,  $\text{ClF}_4\text{O}^+$ , and  $(\text{CF}_3)_2\text{NO}^+$ , respectively. The synthesis of  $(\text{CF}_3)_2\text{NO}^+$ , a potential precursor for the synthesis of a  $\text{CF}_3^+$  group substituted  $\text{ONF}_3$  molecule, was also studied by using  $\text{O}_2^+\text{AsF}_6^-$  as the active oxidizing agent.

A systematic study of low-temperature ozonization reactions was carried out, involving the following starting materials:  $\text{ClOCIO}_3$ ,  $\text{BrOCIO}_3$ ,  $\text{ClO}_2$ ,  $\text{BrOSO}_2\text{F}$ ,  $\text{ClONO}_2$ , and  $\text{ClOSO}_2\text{F}$ . In all cases, the starting materials were successfully oxygenated. Interestingly, the high yield product from the  $\text{ClONO}_2$  ozonization is  $\text{NO}_2^+\text{ClO}_4^-$ .

The reaction chemistry of chlorine perchlorate,  $\text{ClOCIO}_3$ , was further investigated. Attempts were made to synthesize members of the so-far unknown class of

perfluoraryl perchlorates from  $C_6F_5I$  or  $C_6F_5Br$  and  $C10ClO_3$ . In both cases, novel compounds, i.e.,  $C_6F_5I(OC10_3)_2$  and  $(O_3ClO)_2C_6F_5Cl$ , respectively, were obtained.

Efforts were made to synthesize the as-yet unknown halogen heptoxides,  $Br_2O_7$  and  $I_2O_7$ , by reaction of perhalate salts with  $SO_3$ . In the case of  $Cs^+ClO_4^-$ , the known  $Cl_2O_7$ , was indeed obtained in high yield, but for the  $BrO_4^-$  and  $IO_4^-$  salts the isolation of  $Br_2O_7$  and  $I_2O_7$  was not possible owing to complexing with the starting materials.

Covalent fluorosulfates have significant usefulness for chemical synthesis and a number of reaction systems were studied involving iodine, sulfur, and selenium fluorides. In addition, a new and more convenient synthesis of  $S_2O_5F_2$  was found by reacting  $COCl_2$  with  $C10SO_2F$ .

A novel synthesis of  $NF_4^+$  salts was discovered employing uv photolysis. The  $PtF_6^-$ ,  $AsF_6^-$ , and  $BF_4^-$  salts were prepared in this way. A plausible mechanism for the formation and decomposition of  $NF_4^+$  salts is presented which does not require the assumption of  $NF_5$  as an intermediate. Moreover, this study suggests that  $F_2$  in the presence of a strong Lewis acid has an oxidizing power comparable to that of  $PtF_6$ . This enhancement of oxidizing power by a Lewis acid was also demonstrated for  $ClF$  which, in the presence of  $AsF_5$ , can oxidize xenon to the +II oxidation state.

As in the past, a number of structural studies were conducted. Among the compounds studied were  $ClF_4^+$ ,  $BrF_4^+$ ,  $IF_4^+$  and  $SF_5O^-$  salts, trifluoroacetates of iodine,  $SF_4$ ,  $SF_4O$ , and  $Cl_2O_6$ . Our collaboration with other scientists (Professors Sawodny, Edwards, and Naumann) in some of these areas continues, and a new connection was established with Dr. F. Lovas from the National Bureau of Standards, who will carry out a structive determination of  $ClF_3O$  by microwave spectroscopy.

During the past contract year 17 papers were published and an additional 7 manuscripts were submitted and have already been accepted for publication on the work done under this contract.

## INTRODUCTION

This report describes the activities during the past year at Rocketdyne in the area of halogen oxidizer chemistry. As in the past, the research areas were diverse and were both technique and new compound oriented. A large number of compound types were investigated including halogen perchlorate chemistry, halogen oxyfluoride synthesis,  $\text{PtF}_6$  chemistry, new fluorination catalysts, novel energetic cation synthesis, halogen oxide chemistry and halogen fluoride reactions. In addition, pertinent structural data for a number of species were generated. As in the past (Ref. 1 - 4), most of the data have been summarized in manuscript form.

A number of papers also were published or presented which arose from work supported on this program. These are listed below.

## PUBLICATIONS DURING PAST CONTRACT YEAR

### Papers Published

1. "Chlorine Trifluoride Oxide. I. Preparation and Properties." by D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, Inorg. Chem., 11, 2189 (1972).
2. "Chlorine Trifluoride Oxide. II. Photochemical Synthesis," by D. Pilipovich, H. H. Rogers, and R. D. Wilson, Inorg. Chem., 11, 2192 (1972).
3. "Chlorine Trifluoride Oxide, III. Vibrational Spectrum, Force Constants, and Thermodynamic Properties," by K. O. Christe and E. C. Curtis, Inorg. Chem., 11, 2196 (1972).
4. "Chlorine Trifluoride Oxide. IV. Reaction Chemistry," by C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, Inorg. Chem., 11, 2201 (1972).
5. "Chlorine Trifluoride Oxide. V. Complex Formation with Lewis Acids and Bases," by K. O. Christe, C. J. Schack, and D. Pilipovich, Inorg. Chem., 11, 2205 (1972).

6. "Chlorine Trifluoride Oxide. VI. The  $\text{ClF}_4\text{O}^-$  Anion. Vibrational Spectra and Force Constants," by K. O. Christe and E. C. Curtis, Inorg. Chem., 11, 2209 (1972).
7. "Chlorine Trifluoride Oxide, VII. The  $\text{ClF}_2\text{O}^+$  Cation. Vibrational Spectrum and Force Constants," by K. O. Christe, E. C. Curtis, and C. J. Schack, Inorg. Chem., 11, 2212 (1972).
8. "The  $\text{ClO}_2\text{F}_2^+$  Cation," by K. O. Christe, Inorg. Nucl. Chem. Letters, 8, 453 (1972).
9. "Chlorine Trifluoride Dioxide,  $\text{ClF}_3\text{O}_2$ ," by K. O. Christe, Inorg. Nucl. Chem. Letters, 8, 457 (1972).
10. "The  $\text{ClF}_6^+$  Cation," by K. O. Christe, Inorg. Nucl. Chem. Letters, 8, 741 (1972).
11. "On the Reactions of Chlorine Fluorides with Hydroxyl Compounds," by K. O. Christe, Inorg. Chem., 11, 1220 (1972).
12. "Iodine Trisperchlorate and Cesium Tetrapercchlorato Iodate (III)," by K. O. Christe and C. J. Schack, Inorg. Chem., 11, 1682 (1972).
13. "On Alkali Metal Fluoride -  $\text{IF}_5$  Adducts," by K. O. Christe, Inorg. Chem., 11, 1215 (1972).
14. "Vibrational Spectra and Force Constants of the Square Pyramidal Anions,  $\text{SF}_5^-$ ,  $\text{SeF}_5^-$ , and  $\text{TeF}_5^-$ ," by K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, Inorg. Chem., 11, 1679 (1972).
15. "The Tetrafluoroiodate (III) Anion,  $\text{IF}_4^-$ ," by K. O. Christe and D. Naumann, Inorg. Chem., 12, 59 (1973).
16. "A  $^{19}\text{F}$ nmr Study of Chlorine Fluoride Cations," by K. O. Christe, J. F. Hon, and D. Pilipovich, Inorg. Chem., 12, 84 (1973).
17. "Vibrational Spectrum and Force Constants of the  $\text{SF}_5\text{O}^-$  Anion," by K. O. Christe, C. J. Schack, E. C. Curtis, D. Pilipovich, and W. Sawodny, Inorg. Chem., 12, 620 (1973).

Papers in Press (Submitted and Accepted)

18. "Halogen Perchlorates: Additions to Perhaloolefins," by C. J. Schack, D. Pilipovich, and J. F. Hon, Inorg. Chem., 12, 897 (1973).
19. "On the Reaction of  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$  with Xenon, by K. O. Christe and R. D. Wilson, Inorg. Nucl. Chem. Letters.
20. "The Difluoroperchlooyl Cation,  $\text{ClO}_2^+$ ," by K. O. Christe, R. D. Wilson, and E. C. Curtis, Inorg. Chem..
21. "Chlorine Trifluoride Dioxide,  $\text{Cl}_2\text{F}_3\text{O}_2$ ," by K. O. Christe and R. D. Wilson, Inorg. Chem..
22. "The Hexafluorochlorine (VII) Cation,  $\text{ClF}_6^+$ . Synthesis and Vibrational Spectrum," by K. O. Christe, Inorg. Chem..
23. "Vibrational Spectra of Trifluoroacetates," by K. O. Christe and D. Naumann, Spectrochim. Acta.
24. "Chlorine Trifluoride Dioxide Vibrational Spectrum Force Constants, and Thermodynamic Properties," by K. O. Christe and E. C. Curtis, Inorg. Chem..

Papers Presented at Meetings

25. "Chlorine (VII) Fluorides: Preparation, Characterization, and Properties," by K. O. Christe, D. Pilipovich, and R. D. Wilson, 4th European Symposium on Fluorine Chemistry, Ljubljana, Yugoslavia (August 1972).
26. "Inorganic Halogen Oxidizers," by K. O. Christe, invited lectures at the Universities of California, Los Angeles, Riverside, and Berkeley (1972-1973).

## DISCUSSION

### CHLORINE TRIFLUORIDE DIOXIDE

The synthesis of  $\text{ClF}_3\text{O}_2$  from  $\text{FCIO}_2$  and  $\text{PtF}_6$  was successfully scaled up and the reaction parameters were studied. In spite of enormous haniling and purification problems, sufficient amounts of material were prepared to allow the determination of its physical, chemical, spectroscopic, and thermodynamic properties. The results from these studies were summarized in two manuscripts and are presented as Appendixes A and B.

### THE $\text{ClF}_2\text{O}_2^+$ CATION

Two novel  $\text{ClF}_2\text{O}_2^+$  salts,  $\text{ClF}_2\text{O}_2^+\text{AsF}_6^-$  and  $\text{ClF}_2\text{O}_2^+\text{BF}_4^-$  were prepared and characterized by vibrational and  $^{19}\text{F}$ nmr spectroscopy. A modified valence force field was computed for  $\text{ClF}_2\text{O}_2^+$ . Attempts to synthesize the  $\text{ClF}_4\text{O}_2^-$  cation from  $\text{ClF}_3\text{O}_2$  and strong Lewis bases such as  $\text{CsF}$ ,  $\text{FNO}$ , or  $\text{FNO}_2$  were unsuccessful. The results from this study are given in manuscript form in Appendix C.

### THE $\text{ClF}_6^+$ CATION

The investigation of the  $\text{ClF}_6^+$  cation was completed and a detailed manuscript was written (see Appendix D) summarizing Rocketdyne's work. In this manuscript we have also included a vibrational analysis and force constant computations for the  $\text{PtF}_6^-$  and  $\text{IF}_6^-$  anions.

### ON THE EXISTENCE OF $\text{ClF}_5\text{O}$ AND RELATED PHOTOLYSIS REACTIONS

Recently, Zuechner and Glemsen (Ref. 5) claimed the synthesis of  $\text{ClF}_5\text{O}$  by photolysis of  $\text{ClF}_5\text{-OF}_2$  mixtures. However, Rocketdyne studies on this system show quite conclusively that no detectable amounts of  $\text{ClF}_5\text{O}$  are formed in this system. Data on this system are summarized in Appendix E. Because  $\text{ClF}_3\text{O}$  is the main product of the  $\text{ClF}_5\text{-OF}_2$  photolysis,  $\text{BrF}_5\text{-OF}_2$  photolysis also has been studied in more detail.

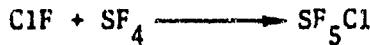
Contrary to  $\text{ClF}_5$ , the  $\text{BrF}_5$  starting material did not react and was recovered unchanged. Similarly, the  $\text{FCIO}_2$ - $\text{OF}_2$  system, when exposed at  $-78^\circ$  to filtered uv-irradiation, did not produce any novel compound.

### SYNTHESIS OF $\text{FCIO}$

The  $\text{ClF}_3\text{O}$ - $\text{SF}_4$  reaction system was studied in an attempt to synthesize  $\text{FCIO}$  according to:



When no catalyst was used, the starting material did not interact at  $-50$  and  $25^\circ\text{C}$ . In the presence of  $\text{CsF}$ , however, the following products were obtained:  $\text{SF}_6$ ,  $\text{SF}_5\text{Cl}$ ,  $\text{SF}_4\text{O}$ , and  $\text{FCIO}_2$ . These results indicate that the desired reaction may have initially occurred, but was followed by:



In addition, a competing reaction, i.e., oxygenation of  $\text{SF}_4$  to  $\text{SF}_4\text{O}$ , must have occurred to a lesser extent. This finding, i.e., the ready disproportionation of  $\text{FCIO}$  to  $\text{FCIO}_2$  and  $\text{ClF}$ , was recently confirmed by Cooper *et al.* (Ref. 6). They studied the hydrolysis of  $\text{ClF}_3$  in a flow reactor and obtained infrared spectroscopic evidence for an unstable intermediate which rapidly decomposed to  $\text{FCIO}_2$  and  $\text{ClF}$ .

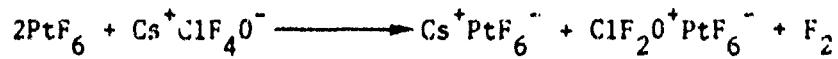
### SYNTHESIS OF $\text{ClF}$

The reaction parameters were studied for the synthesis of  $\text{ClF}$  from  $\text{ClF}_3$  and  $\text{Cl}_2$ . It was found that  $\text{ClF}$  can be prepared in almost quantitative yield at temperatures as low as  $150^\circ\text{C}$ . The results are summarized in manuscript form in Appendix F.

## PtF<sub>6</sub> REACTION CHEMISTRY

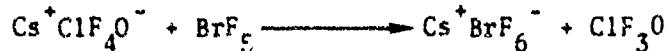
Because PtF<sub>6</sub> has proved to be such a useful fluorinating oxidizer for the synthesis of ClF<sub>3</sub>O<sub>2</sub>, ClF<sub>2</sub>O<sub>2</sub><sup>+</sup>, and ClF<sub>6</sub><sup>+</sup>, its reaction chemistry has been under continuing study. A logical extension of the ClF<sub>6</sub><sup>+</sup> synthesis was the attempt to prepare BrF<sub>6</sub><sup>+</sup> salts. However, in the BrF<sub>5</sub>-PtF<sub>6</sub> system at 25 C, no reaction occurs between BrF<sub>5</sub> and PtF<sub>6</sub>. Using unfiltered uv irradiation, PtF<sub>6</sub> decomposes to lower platinum fluorides and F<sub>2</sub>, but no BrF<sub>6</sub><sup>+</sup> salt is formed. The ternary system, FC1O<sub>2</sub>-BrF<sub>5</sub>-PtF<sub>6</sub>, was also investigated. Upon melting of the halogen fluorides, a rapid reaction occurs, producing exclusively ClO<sub>2</sub><sup>+</sup>PtF<sub>6</sub><sup>-</sup> and F<sub>2</sub>, but no BrF<sub>6</sub><sup>+</sup>. The third system, Cs<sup>+</sup>BrF<sub>6</sub><sup>-</sup>+BrF<sub>5</sub> + PtF<sub>6</sub>, was kept at 25C for 93 days. Analysis of the products showed no evidence for the desired BrF<sub>6</sub><sup>+</sup> cation, but indicated the formation of some Cs<sup>+</sup>PtF<sub>6</sub><sup>-</sup> and PtF<sub>5</sub> as only new products.

Much effort was concentrated on the synthesis of ClF<sub>4</sub>O<sup>+</sup> salts, which would allow the synthesis of the new and very desirable compound ClF<sub>5</sub>O. Because the reaction of PtF<sub>6</sub> with ClF<sub>3</sub>O in the absence of a solvent had to be carried out above -42 C (m.p. of ClF<sub>3</sub>O) and yielded only ClF<sub>2</sub>O<sup>+</sup>PtF<sub>6</sub><sup>-</sup> and F<sub>2</sub>, this system has been studied in a low melting solvent. An ideal inert solvent was found with FC1O<sub>3</sub> which melts at about -150 C, has a high solubility for PtF<sub>6</sub>, and is completely inert to PtF<sub>6</sub>. Two reactions of ClF<sub>3</sub>O with PtF<sub>6</sub> were carried out in FC1O<sub>3</sub> solution, differing in the warm-up conditions. In both cases, again only ClF<sub>2</sub>O<sup>+</sup>PtF<sub>6</sub><sup>-</sup> and F<sub>2</sub>, but no ClF<sub>4</sub>O<sup>+</sup>, were obtained. Because previous attempts to prepare either ClF<sub>4</sub>O<sup>+</sup> or ClF<sub>5</sub>O directly from ClF<sub>3</sub>O and PtF<sub>6</sub> were unsuccessful (see Appendix D), the reaction of Cs<sup>+</sup>ClF<sub>4</sub>O<sup>-</sup> with PtF<sub>6</sub> was studied in the presence and absence of a solvent. Without any solvent and using ultrasonic mixing, solid Cs<sup>+</sup>ClF<sub>4</sub>O<sup>-</sup> interacted with PtF<sub>6</sub> at 25 C within 48 hours quantitatively, according to:



Using FC1O<sub>3</sub> as a solvent, the reaction of PtF<sub>6</sub> was much faster and proceeded at a lower temperature. However, the reaction products were identical to those given above. The possibility of using BrF<sub>5</sub> as a solvent was also examined. It was

found to be incompatible with  $\text{Cs}^+\text{ClF}_4^-$ , owing to the following quantitative displacement reaction:

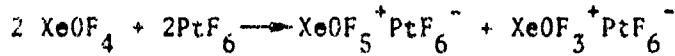


Another desirable, energetic species would be the  $\text{OF}_3^+$  cation. It is isoelectronic with  $\text{NF}_3$  and, hence, might possess a reasonable stability. In its attempted synthesis, a mixture of  $\text{OF}_2$  and  $\text{PtF}_6$  was kept for 100 days in a sapphire reactor at 25 C. While all of the  $\text{PtF}_6$  was consumed, all of the  $\text{OF}_2$  was recovered unreacted. Based on the observed weight changes and the infrared spectrum of the solid residue, the following interaction between the reactor and  $\text{PtF}_6$  occurred:



The reaction of ozone and  $\text{PtF}_6$  has also been investigated for the possible formation of  $\text{O}_3^+\text{PtF}_6^-$ . The  $\text{O}_3^+$  cation might exist, being isoelectronic with  $\text{NO}_2$ . During several weeks reaction at temperatures of -80 to -45 C, it was found that very little  $\text{O}_3$  reacted and nearly all was recoverable. Thus, it appears that the  $\text{PtF}_6$  has a stabilizing effect on  $\text{O}_3$  under these conditions. At ambient temperature,  $\text{O}_3$  and  $\text{PtF}_6$  gave a nearly quantitative yield of  $\text{O}_3^+\text{PtF}_6^-$ . This was based both on the amount of excess  $\text{O}_3$  recovered and the weight increase of the  $\text{PtF}_6$ . Thus,  $\text{O}_3^+\text{PtF}_6^-$  does not appear to be preparable in this manner.

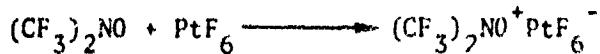
Since  $\text{PtF}_6$  can oxidize  $\text{ClF}_5$  to  $\text{ClF}_6^+$  and since  $\text{XeOF}_4$  is pseudo-isoelectronic with  $\text{ClF}_5$ , it might be possible to prepare  $\text{XeOF}_5^+$  according to:



The first attempt to synthesize the  $\text{XeOF}_4$  starting material according to a literature report by hydrolysis of  $\text{XeF}_6$  came to an explosive halt. In the meantime, several grams of  $\text{XeOF}_4$  were prepared by the alternate procedure based on the slow interaction between  $\text{XeF}_6$  and quartz. In addition, a  $\text{PtF}_6$  preparation, which in the past has successfully been carried out many times, failed owing to

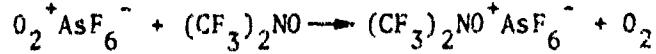
burn out. As soon as new platinum wire is received, this study will be resumed.

Reactions of  $\text{PtF}_6$  with free nitroxide radicals such as  $(\text{CF}_3)_2\text{NO}$  were investigated with the intent of achieving the synthesis of a novel  $\text{CF}_3$  substituted  $\text{NF}_3\text{O}$  molecule, according to:



The nitroxide starting materials were synthesized and allowed to interact with  $\text{PtF}_6$  at the lowest poss. 1e temperature. However, in all cases the reaction was so violent (confined explosions) that the only products obtained were  $\text{NO}^+\text{PtF}_6^-$ ,  $\text{CF}_4$ ,  $\text{COF}_2$ ,  $\text{CF}_3\text{NO}_2$ ,  $(\text{CF}_3)_2\text{NOCF}_3$ , and small amounts of  $\text{NF}_3$ . It is planned to repeat these reactions in the future using the milder oxidizers  $\text{ReF}_6$  or  $\text{MoF}_6$  in place of  $\text{PtF}_6$ .

The reaction of  $\text{O}_2^+\text{AsF}_6^-$  with  $(\text{CF}_3)_2\text{NO}$  at low temperature was also studied as an alternate route to  $(\text{CF}_3)_2\text{NO}^+$  salts:



However, the solid was shown to be  $\text{NO}^+\text{AsF}_6^-$  and  $\text{COF}_2$  and  $\text{CF}_4$  were obtained as volatile products. This indicates that  $(\text{CF}_3)_2\text{NO}^+$  may have initially formed, but is unstable. This experiment will be repeated at a lower temperature, substituting  $\text{O}_2^+\text{AsF}_6^-$  with the more stable salt  $\text{O}_2^+\text{SbF}_6^-$ . The latter starting material was synthesized from  $\text{O}_2 + \text{F}_2 + \text{SbF}_5$ .

## OZONE OXIDATIONS

Compounds containing the terminal haloxy group,  $XO^-$ , are uniformly reactive and utilitarian reagents. However, nearly all of the known chemistry of these materials centers on their reaction through cleavage of the haloxy bond, e.g., the use of  $ClOSO_2F$  to produce  $ClOClO_3$  from  $Ag^+ClO_4^-$  (Ref. 3) and the use of  $ClOClO_3$  to prepare  $ClO_2COClO_3$  compounds (Ref. 3). To change the nature of these  $XO^-$  moieties and thus perhaps to change their types of reactivity and stability, studies were aimed at the oxidative oxygenation of the terminal halogen.

The only report of such an oxidation was given by Schmeisser and Taglinger (Ref. 7). They reported the ozonization of  $BrONO_2$  at -78°C as shown in the equation:

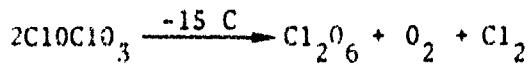


The good results realized in that system offered promise of equally useful reactions with other  $XO^-$  species. Of immediate interest were the halogen perchlorates,  $ClOClO_3$  and  $BrOClO_3$ . In the case of  $ClOClO_3$  it was found that oxidation via ozonization occurred under a variety of conditions according to the equation:



At -80°C the reaction was slow, providing only a 35-percent yield of  $Cl_2O_6$  after more than a 24-hour reaction. At -45°C the reaction was studied with and without  $CF_3Cl$  as a solvent. In the former case, and using excess  $ClOClO_3$ , an 80-percent yield of  $Cl_2O_6$  based on  $O_3$ , was obtained with the unreacted  $ClOClO_3$  being recovered. Thus, an even higher conversion of the reacted  $ClOClO_3$  was realized. Without the solvent, but with a slight excess of  $O_3$  over the required 2:1 ratio, a virtually quantitative formation of  $Cl_2O_6$  was achieved.

To prove the identity of the chlorine oxide produced by this reaction and that reported for  $\text{Cl}_2\text{O}_6$ , alternative syntheses were carried out. One of these involved the slow degradation of  $\text{ClOClO}_3$  in the dark (Ref. 8):



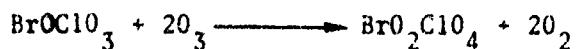
Another employed the usual ozonization of chlorine dioxide (Ref. 9):



When this ozonization was run at -45 C, it was found that  $\text{Cl}_2\text{O}_6$  was formed at a faster rate than with  $\text{ClOClO}_3$  as a substrate. In all respects -- appearance, vapor pressure, composition, and mass spectra -- the  $\text{Cl}_2\text{O}_6$  from each of these sources was the same and no indication of isomeric forms of  $\text{Cl}_2\text{O}_6$  was noted.

Some disagreement regarding the mass spectrum of  $\text{Cl}_2\text{O}_6$  exists. Cordes and Smith (Ref. 10) observed a weak  $\text{ClO}_3^+$  ion as the highest m/e from  $\text{Cl}_2\text{O}_6$ . However, Fisher (Ref. 11) found no  $\text{ClO}_x^+$  ions above  $\text{ClO}_2^+$ , but his samples showed appreciable  $\text{HCIO}_4$  impurity. In Rocketdyne's work, samples without  $\text{HCIO}_4$  gave a small (5-percent of base) peak for  $\text{ClO}_3^+$ . Even samples with some  $\text{HCIO}_4$  exhibited a modest but reproducible  $\text{ClO}_3^+$  peak when the spectrum was corrected for that impurity.

The novel process for ozonizing the terminal chlorine of  $\text{ClOClO}_3$  was applied to  $\text{BrOCIO}_3$ . Surprisingly, it was found that neat  $\text{O}_3$  and  $\text{PrOCIO}_3$  in the temperature range of -80 to -45 C reacted to cause their complete degradation to the elements. An effort was therefore made to moderate the reaction through the use of  $\text{CF}_3\text{Cl}$  as a solvent. This was successful and the reaction observed at -45 C was:

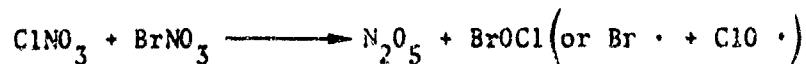


Excellent oxygen balance for this stoichiometry was realized and confirmed by analysis of the product. This showed that  $3\text{O}_2$  was present for each  $\text{BrCl}$  in the molecule.

The new composition,  $\text{BrO}_2\text{ClO}_4$ , is a bright orange solid that does not melt up to at least -40 C. Decomposition at room temperature occurs slowly in well-passivated metal. Efforts to further characterize and utilize the compound are in progress. An attempt to displace  $\text{FBrO}_2$  using  $\text{FNO}_2$  was unsuccessful since only a small amount of  $\text{FNO}_2$  reacted.

In view of the failure to secure a controlled reaction of  $\text{O}_3$  and  $\text{BrOClO}_3$  in the absence of a solvent, it was not unexpected that  $\text{BrOSO}_2\text{F}$  would behave similarly. Thus, it was determined that neat  $\text{O}_3$  and  $\text{BrOSO}_2\text{F}$  did not produce an ozonization product. Instead, all the  $\text{O}_3$  was decomposed to  $\text{O}_2$  and most of the  $\text{BrOSO}_2\text{F}$  degraded to  $\text{Br}_2$ ,  $\text{SO}_2\text{F}_2$  and  $\text{S}_2\text{O}_5\text{F}_2$ . Results of solution ozonization of  $\text{BrOSO}_2\text{F}$  are not in hand as yet.

Bromine nitrate was also sought for use in the ozone oxidation studies. Its synthesis from  $\text{Br}_2$  and  $\text{ClNO}_3$  (Ref. 7) at -45 C was extremely sluggish. Also, long reaction times were ineffective because of an apparent degrading reaction which produced  $\text{Br}_2$ ,  $\text{ClO}_2$ , and  $\text{N}_2\text{O}_5$ . The formation of these products probably occurs through a competitive and previously unsuspected interaction of  $\text{BrNO}_3$  and  $\text{ClNO}_3$ , as shown by the equations:



Alternate routes to  $\text{BrNO}_3$  are being investigated.

An initial attempt to effect the ozonization of  $\text{ClONO}_2$  at -80°C without a solvent indicated no reaction occurred. With  $\text{CF}_3\text{Cl}$  as a solvent, at either -80 or -45°C, a successful oxidation was achieved as shown:



Yields of  $\text{NO}_2^+ \text{ClO}_4^-$  on the order of 80- to 90-percent are routinely obtainable. This reaction represents a new process for preparing nitronium perchlorate and avoids the use of the troublesome  $\text{ClO}_2$  which is commonly employed as part of that synthesis (Ref. 9).

Chlorine fluorosulfate was expected to undergo oxidative ozonization since a predicted product,  $\text{ClO}_2\text{SO}_3\text{F}$ , is known from other synthetic schemes (Ref. 9 and 12). It was found that no solvent was required to produce the reaction:



A moderate reaction occurred even at 0°C furnishing 70- to 90-percent yields of chloryl fluorosulfate. Further oxygen up-take beyond this composition was not observed.

#### CHLORINE PERCHLORATE REACTIONS

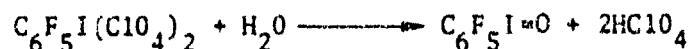
Several examples of the synthesis of the previously unknown class of compounds, perchloroalkylperchlorates, were discovered on this program (Ref. 3) through the use of chlorine perchlorate. More examples were obtained recently under another program (Ref. 13). However, no examples of aromatic perchlorates have been reported and it was of interest to ascertain whether  $\text{Cl}_2\text{O}_4$  would be useful in this regard. Iodopentafluorobenzene was selected as a test vehicle. Reaction at -45°C produced excellent volumetric and gravimetric data in accordance with the equation:



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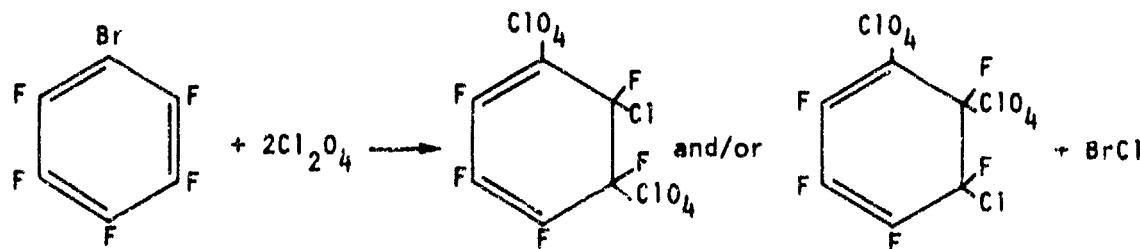
The perchlorate product is a shiny, pale yellow solid completely stable at ambient temperature and nonvolatile. It is probably similar to  $I(CIO_4)_3$  (Ref. 2) or  $(CF_3)_2CFI(CIO_4)_2$  (Ref. 13), although this stoichiometry does not rule out a composition such as  $(C_6F_5)_2I^+I(CIO_4)_4^-$  as was found for the compound  $(C_4F_9)_2I^+IF_6^-$  (Ref. 14). Retention of the aromatic character of the ring was shown by the infrared spectrum which also showed the presence of perchlorate groups.

Although thermally stable, the solid is either friction or impact sensitive. Thus, while attempting to break up a lump of this solid with a metal spatula, it exploded. While insoluble in water, the solid is slowly hydrolyzed, producing a pale yellow powder.



The identity of the iodoso derivative was confirmed by comparison of its infrared and melting point to that given in the literature (Ref. 15). Investigation and characterization of this new perchlorate is continuing.

When the reaction of  $C_6F_5Br$  and  $Cl_2O_4$  was examined at  $-45^\circ C$ , a different result was obtained. Again, two moles of  $Cl_2O_4$  reacted for each mole of the aryl compound. However, displacement of the bromine was accomplished as evidenced by the evolution of  $BrCl$ . Nevertheless, the product was not a simple  $R_fClO_4$  moiety. After pumping for several hours at  $0^\circ C$  to room temperature, there remained a colorless, slightly viscous liquid. The by-products observed and the weight of the product indicated a composition for this liquid of  $(ClO_4)_2C_6F_5Cl$ . The infrared spectrum of the neat liquid revealed very strong covalent  $ClO_4$  group bands but no  $1500\text{ cm}^{-1}$  aromatic ring band. These results indicate the probable reaction to be:



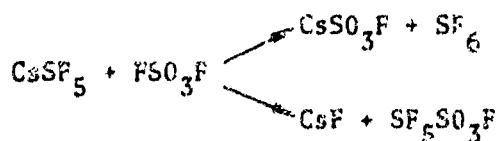
The mass spectrum of the liquid confirms the lack of aromatic character for the liquid. Moreover, ion peaks for fragments such as  $C_4F_3Cl_2O^+$ ,  $C_3F_3Cl_2O^+$ ,  $C_3F_2ClO^+$ , and  $C_2F_2ClO^+$  tend to support the above formulation. However, there appears to be an abnormally high number of peaks tentatively assigned to saturated molecular fragments such as  $CFC_1^+$  and  $CF_2Cl^+$ . Also, the infrared spectrum shows a strong band near  $1870\text{ cm}^{-1}$ . Typically, such a band is due to the  $C=O$  stretching mode of an  $R_fC(0)F$  species. If such were the case here, then it would mean the aromatic ring had been opened. Additional spectral investigations including  $^{19}F$  nmr are planned to resolve these points.

#### HALOGEN HEPTOXIDES

New approaches for the synthesis of  $Cl_2O_7$  from perchlorate salts were studied. These will be applied to the syntheses of the as-yet unknown heptavalent halogen oxides  $Br_2O_7$  and  $I_2O_7$ . We found that  $Cl_2O_7$  can be prepared from  $Cs^+ClO_4^-$  and  $SO_3$  in high yield. Extension of this reaction to  $Cs^+BrO_4^-$  and  $K^+IO_4^-$  resulted in interaction of the starting materials; however, the products appeared to form adducts and could not be isolated and characterized without decomposition to the elements. Further experiments are planned in which  $SO_3$  will be substituted by the more volatile  $FSO_2$ - $SO_2F$ . This should facilitate the product workup. The new  $Br_2O_7$  and  $I_2O_7$  species would be excellent candidates for high detonation pressure explosives.

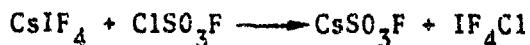
#### COVALENT FLUOROSULFATE STUDIES

The covalent inorganic fluorosulfates have significant synthetic usefulness and a number of reaction systems were studied involving iodine, sulfur, and selenium fluorides. Fluorine fluorosulfate and  $CsSF_5$  were reacted to determine which of two possible reaction paths would be followed.

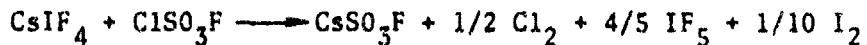


As has often been noted with the other halogen fluorosulfates, the tendency to form the fluorosulfate ion predominates and, accordingly, the upper path was followed exclusively. While all the  $\text{FSO}_3\text{F}$  that reacted liberated  $\text{SF}_6$ , not all the  $\text{FSO}_3\text{F}$  or  $\text{CsSF}_5$  reacted. A 55-percent conversion of the available  $\text{SF}_5^-$  was achieved.

Chlorine fluorosulfate has repeatedly demonstrated an ability to serve as a source of positively polarized chlorine in converting anions to covalent species. An attempt to utilize this property was made with the goal of forming  $\text{IF}_4\text{Cl}$  as indicated by the equation

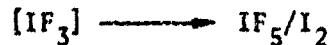
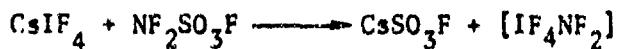


Despite the use of a maximum reaction temperature of -80°C, it was found that  $\text{Cl}_2$  was quantitatively released at that temperature. At higher temperatures the co-products  $\text{IF}_5$  and  $\text{I}_2$  were found leaving a residue of  $\text{CsSO}_3\text{F}$ . The indicated stoichiometry is:



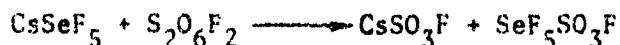
Perhaps  $\text{IF}_4\text{Cl}$  was formed, but it was certainly unstable even at -80°C.

In a similar manner,  $\text{NF}_2\text{SO}_3\text{F}$  was reacted with  $\text{CsIF}_4$  in an effort to make the substituted  $\text{IF}_5$  derivative,  $\text{IF}_4\text{NF}_2$ . With excess  $\text{CsIF}_4$ , a prolonged reaction at -45°C did not consume all the  $\text{NF}_2\text{SO}_3\text{F}$ . However, no  $\text{IF}_4\text{NF}_2$  was detected, but only  $\text{IF}_5/\text{I}_2$  and  $\text{SO}_2\text{F}_2$ . The apparent reaction sequence is:

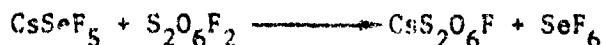


Nitrogen trifluoride was not observed but it would have been pumped away in the course of the work-up procedure used. The  $\text{SO}_2\text{F}_2$  arose from the fluorination of  $\text{SO}_2$  which was an impurity in the  $\text{NF}_2\text{SO}_3\text{F}$ . It seems certain that  $\text{IF}_4\text{NF}_2$  is incapable of synthesis in this manner.

Peroxydisulfuryl difluoride was reacted with the salt,  $\text{CsSeF}_5$ , with the expectation that a simple fluorosulfonation would occur.

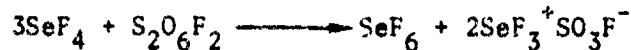


Reaction at ambient temperature did not occur in this manner, however. Instead the exclusive reaction was the fluorination process represented by the equation:



The fluorodisulfate anion is not especially well known and only one other example of its formation from  $\text{S}_2\text{O}_6\text{F}_2$  is known to Rocketdyne (Ref. 16). That synthesis entailed the fluorination of peroxydisulfate salts with  $\text{S}_2\text{O}_6\text{F}_2$ .

In contrast to this result, the interaction of  $\text{S}_2\text{O}_6\text{F}_2$  and  $\text{SeF}_4$  did proceed via cleavage of the peroxy bond but again fluorination was encountered. The observed ambient temperature reaction was:



This constitutes a new synthesis of this salt which was previously prepared (Ref. 17) from  $\text{SeF}_4$  and  $\text{SO}_3$ . Compared to the  $\text{SF}_4 + \text{S}_2\text{O}_6\text{F}_2$  reaction (Ref. 18) which yields  $\text{SF}_4(\text{SO}_3\text{F})_2$ , the tendency of the aluminum fluorides to undergo fluorination is remarkable.

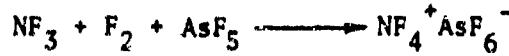
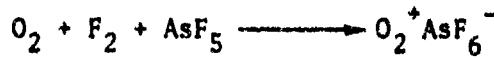
Among the useful properties of chlorine fluorosulfate is its ability to serve as a precursor for other covalent inorganic fluorsulfates. This has led to its use (Ref. 19) in preparing  $\text{S}_2\text{O}_6\text{F}_2$  and  $\text{BrSO}_3\text{F}$ , for example. Another such synthetic application was found in the following reaction:



Pyrosulfuryl fluoride can be obtained in at least 90 percent yield and quickly by this process. Purification is simple since the by-product  $\text{CO}_2$  and  $\text{Cl}_2$  are appreciably more volatile.

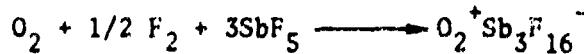
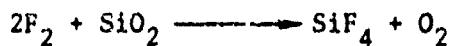
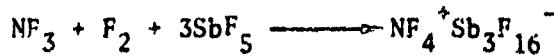
## $\text{NF}_4^+$ CHEMISTRY

A new synthesis of  $\text{NF}_4^+$  salts has been discovered at Rocketdyne. When mixtures of  $\text{NF}_3$ ,  $\text{F}_2$ ,  $\text{AsF}_5$  or  $\text{NF}_3$ ,  $\text{F}_2$ ,  $\text{BF}_3$  at 200-psi pressure in a sapphire reactor were exposed to uv radiation, the solids  $\text{NF}_4^+\text{AsF}_6^-$  and  $\text{NF}_4^+\text{BF}_4^-$ , respectively, were formed. It was shown that in the absence of light, no reaction occurs, and that based on the observed rates, the  $\text{NF}_4^+\text{AsF}_6^-$  formation must be a chain reaction. Rationalization of the following reaction systems led to the conclusion that the common reactive intermediate must be the  $\text{AsF}_6^-$  radical having an oxidizing power comparable to that of  $\text{PtF}_6$  (>12 ev).



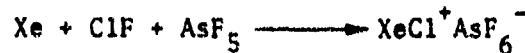
A plausible mechanism was written for both the formation and thermal decomposition of  $\text{NF}_4^+$  salts. Contrary to the mechanism suggested by I. Solomon of IITRI, the Rocketdyne mechanism does not require formation of the energetically unfavorable  $\text{NF}_5$  molecule as an intermediate. These results are summarized in Appendix G.

In addition, the photolysis of  $\text{NF}_3 - \text{F}_2 - \text{SbF}_5$  has been studied at a 1-atmosphere pressure in a quartz bulb. Within several days, all of the  $\text{SbF}_5$  was converted to a white solid, which was shown to be an equimolar mixture of  $\text{NF}_4^+\text{Sb}_3\text{F}_{16}^-$  and  $\text{O}_2^+\text{Sb}_3\text{F}_{16}^-$  in agreement with the following equations:

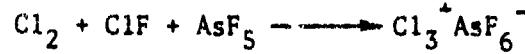
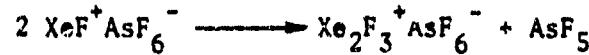
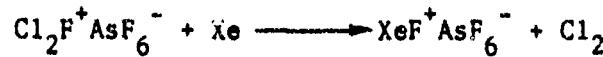
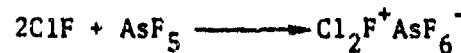


## OXIDATION OF XENON BY $\text{Cl}_2\text{F}^+\text{AsF}_6^-$

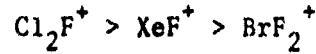
The  $\text{Xe}$ ,  $\text{ClF}$ ,  $\text{AsF}_5$  system was studied as a model reaction for the heterolytic fission of  $\text{ClF}$  according to:



However, the following competing reactions occurred:



These results demonstrate that  $\text{Cl}_2\text{F}^+$  is a stronger oxidizer than  $\text{ClF}_3$  or  $\text{ClF}$ , both of which do not oxidize  $\text{Xe}$ , and establish the following order of oxidizing power:



Results from this study were summarized in manuscript form (Appendix H).

## STRUCTURAL STUDIES

The vibrational spectra of the following halogen pentafluoride-Lewis acid adducts were recorded:  $\text{ClF}_4^+\text{SbF}_6^-$ ,  $\text{ClF}_4^+\text{AsF}_6^-$ ,  $\text{BrF}_4^+\text{Sb}_2\text{F}_{11}^-$ , and  $\text{IF}_4^+\text{SbF}_6^-$ . Complete force constant ellipses were computed for the  $\text{ClF}_4^+$  cation. In addition, the  $^{19}\text{F}$  nmr spectra of these adducts were studied in HF solution. Results are given in Appendix I.

To be able to assign the  $\text{ClF}_4^+$  spectrum, it was necessary to clarify the existing discrepancies for isoelectronic  $\text{SF}_4$  by force constant and mean square amplitudes of vibration computations. The results are summarized in Appendix J.

Because the vibrational spectra of chlorine fluorides or oxyfluorides were found to closely resemble those of the isoelectronic sulfur compounds, we studied the spectrum of  $SF_5O^-$ . This anion is isoelectronic with  $ClF_5O$ , an as-yet unprepared oxidizer in which we have much interest. The results from this study are given in Appendix K. For the same reason, an investigation was begun on the vibrational spectrum of  $SF_4O$  which is isoelectronic with the as-yet unknown  $ClF_4O^+$  cation. This study is still in progress and the results will be presented in a future report.

Rocketdyne has conducted studies on the structure of the  $CsI(O_2CCF_3)_4$  and  $Cs_3^+ (O_2CCF_3)_6$  adducts by infrared and Raman spectroscopy and by X-ray powder diffraction techniques. It was shown that the trifluoroacetate group forms a highly polarized covalent bond with iodine. The results from this study are summarized in Appendix L.

A strong effort was made to establish the structure of free dichlorine hexoxide by both matrix isolation and mass spectroscopic techniques. Unfortunately,  $Cl_2O_6$  decomposes in the gas phase extremely rapidly to  $ClO_2$  and oxygen. Consequently, no clear-cut evidence for either covalent chloryl perchlorate present in its ionic form in solid  $Cl_2O_6$  (Ref. 20) or for the  $ClO_3$  radical could be obtained. Two novel species were observed, but could not be identified conclusively.

A sample of  $ClF_3O$  was prepared, purified, and shipped to Dr. F. Lovas of the National Bureau of Standards where a structure determination will be conducted using microwave spectroscopy.

## EXPERIMENTAL

### PREPARATION OF OZONE

Ozone was prepared by electric discharge of  $O_2$  in a Pyrex U-tube cooled with liquid nitrogen. A 15-kv power supply through internal copper electrodes provided the discharge. Upon conversion of a charge of  $O_2$  to  $O_3$  (which was easily followed manometrically), the discharge was stopped and the  $O_3$  was transferred to the vacuum line. After expanding and measuring the  $O_3$  in the line, it was immediately loaded into a precooled reactor. Somewhat more than one millimole of pure  $O_3$  was obtained from each batch. Larger quantities could be easily prepared but would, of course, not be as safe to handle.

### OZONIZATION OF CHLORINE PERCHLORATE

Freshly prepared (Ref. 8) and purified chlorine perchlorate (1.35 millimole) was condensed into a prepassivated, 30-milliliter stainless-steel cylinder cooled to -196 C. To the same cylinder, freshly prepared  $O_3$  (2.86 millimoles) was subsequently added. The reaction was allowed to proceed by warming and maintaining the reactor at approximately -45 C for 2 days or longer. At that time, recooling to -196 C showed  $O_2$  was present as indicated by its vapor pressure. The oxygen was pumped from the reactor and measured (2.96 millimoles). Additional pumping on the reactor, while warming to -45 C, produced less than 1 cc of condensable materials. Thus all the  $Cl_2O_4$  had reacted with sufficient  $O_3$ , as indicated by the by-product  $O_2$ , producing  $Cl_2O_6$ . The identity of the  $Cl_2O_6$  was established by its elemental analysis after decomposition at elevated temperature. Thus from 1.35 millimole of  $Cl_2O_6$  there was obtained 1.33 millimole  $Cl_2$  and 3.95 millimole  $O_2$ . Furthermore, transferring this product to a Teflon U-trap on the vacuum line showed it to have the same physical appearance and properties described for  $Cl_2O_6$  synthesized by other processes (Ref. 9). It was a very dark red liquid or solid, melting near 0 C and exhibiting only several mm vapor pressure near ambient temperature. On standing at ambient temperature, slow bubbling within the sample was noted and the gas pressure increased gradually. This was found to be caused by the formation of  $ClO_2$ ,  $Cl_2$ , and  $O_2$ , resulting from the decomposition of the  $Cl_2O_6$ .

## OZONIZATION OF CHLORINE DIOXIDE

Chlorine dioxide was prepared from  $\text{NaClO}_2$  and  $\text{Cl}_2$  (Ref. 21) at -45 C and purified by fractional condensation. The ozonation of  $\text{ClO}_2$  is the favored method for synthesizing  $\text{Cl}_2\text{O}_6$  (Ref. 9). The procedure followed at Rocketdyne was identical to that described previously for the  $\text{Cl}_2\text{O}_4-\text{O}_3$  reaction. After an 18-hour reaction at -45 C, 1.26 millimole of  $\text{ClO}_2$  and 3.16 millimoles of  $\text{O}_3$  yielded 1.85 millimole of unreacted  $\text{O}_3$  and 1.34 millimole of  $\text{O}_2$ . This indicated 1.30 millimole of atomic oxygen had been taken up in good agreement with the reported stoichiometry for the reaction. Essentially, a quantitative conversion to  $\text{Cl}_2\text{O}_6$  was confirmed by the failure to recover any  $\text{ClO}_2$  or other by-products. The product  $\text{Cl}_2\text{O}_6$  was as described in the literature.

## OZONIZATION OF BROMINE PERCHLORATE

Bromine perchlorate was prepared in reactors in which subsequent ozonation could be performed without transferring the  $\text{BrClO}_4$ . Thus decomposition of  $\text{BrClO}_4$  through handling was avoided. The reaction of  $\text{Br}_2$  and  $\text{Cl}_2\text{O}_4$  was used to synthesize  $\text{BrClO}_4$  (Ref. 22). A 1.29-millimole sample of  $\text{BrClO}_4$  and 3.06 millimoles of  $\text{O}_3$  were reacted at -45 C in the presence of 12 millimoles of  $\text{CF}_3\text{Cl}$  solvent. After several days the mixture was recooled to -196 C and the by-product  $\text{O}_2$  (3.26 millimoles) was measured indicating one mole of  $\text{O}_2$  was taken up per mole of  $\text{BrClO}_4$  present. The solvent was removed by warming and pumping, and finally the sample was pumped on for an hour at -45 C. Only the solvent,  $\text{CF}_3\text{Cl}$ , was observed among the volatile species. Analysis of the indicated  $\text{BrO}_2\text{ClO}_4$  product was obtained by decomposition of the sample at 90 C for several hours. From the 1.29 millimole of  $\text{BrO}_2\text{ClO}_4$  was obtained 1.28 millimole of a mixture of  $\text{Cl}_2$ ,  $\text{BrCl}$ , and  $\text{Br}_2$  which was identified by its mass spectrum. In addition, 3.97 millimoles of  $\text{O}_2$  were obtained. Thus, the product contained  $\text{BrCl}$  and  $\text{O}_2$  in the ratio 1.00:3.07. Bromyl perchlorate samples prepared in sapphire reactors were observed to be bright orange solids that did not melt to about -40 C. Decomposition to the elements also occurred at ambient temperature over several days.

### OZONIZATION OF BROMINE FLUOROSULFATE

Bromine fluorosulfate was prepared from  $\text{Br}_2$  and  $\text{ClSO}_3\text{F}$  in a 30-milliliter cylinder. After purification by removal of by-product  $\text{Cl}_2$  and excess  $\text{ClSO}_3\text{F}$ , ozone (3.37 millimoles) was added to the  $\text{BrSO}_3\text{F}$  (1.25 millimole) at -196 C. The reactor was allowed to warm very slowly to -45 C by placing it into a liquid  $\text{N}_2\text{-CO}_2$  slush bath that was permitted to evaporate in a -45 C chamber. After 6 days, recocling to -196 C revealed all the  $\text{O}_3$  had decomposed and part of the  $\text{BrSO}_3\text{F}$  to give 5.14 millimoles of  $\text{O}_2$ . Further evidence for partial decomposition of the  $\text{BrSO}_3\text{F}$  was the discovery of  $\text{SO}_2\text{F}_2$ ,  $\text{S}_2\text{O}_5\text{F}_2$ , and some  $\text{Br}_2$  by fractional condensation of the -45 C volatile products. Additional fractionation led to the recovery of  $\text{BrSO}_3\text{F}$  only and no other product.

### OZONIZATION OF CHLORINE NITRATE

Chlorine nitrate (1.03 millimole) prepared from  $\text{ClF}$  and  $\text{HNO}_3$  (Ref. 23) was loaded into a 30-milliliter cylinder at -196 C followed by  $\text{CF}_3\text{Cl}$  solvent (21 millimoles) and  $\text{O}_3$  (4.04 millimoles). The reaction was then allowed to proceed at -45 C for several days. At that time the  $\text{O}_2$  present was measured (4.73 millimoles) and removed together with the solvent. The latter had a faint yellow color but no infrared absorbances other than those of  $\text{CF}_3\text{Cl}$  itself, thus indicating some  $\text{Cl}_2$  as an impurity. Finally, the cylinder was pumped on at room temperature for 30 minutes before weighing.

The nonvolatile residue, a white fluffy powder, weighed 13.5 milligrams and was identified as  $\text{NO}_2^+\text{ClO}_4^-$  by its infrared spectrum (Ref. 24). This yield of 0.92 millimole was 89 percent of theory.

### OZONIZATION OF CHLORINE FLUOROSULFATE

Chlorine fluorosulfate (1.06 millimole) prepared from  $\text{ClF}$  and  $\text{SO}_3$  (Ref. 19) was condensed into a 10-milliliter cylinder cooled with liquid  $\text{N}_2$ , followed by  $\text{O}_3$  (2.30 millimoles). After reaction at -45 C for several days, the -196 C non-condensable gas,  $\text{O}_2$ , which had formed was measured (2.44 millimoles) and removed.

Warming to -45 C while pumping liberated about 1 cc of -196 C condensable material. Thus, nearly all the  $\text{ClSO}_3\text{F}$  had reacted producing  $\text{ClO}_2\text{SO}_3\text{F}$  in 97 yield (1.03 millimole). The product is a low-volatility dark red liquid (Ref. 12).

#### REACTION OF $\text{Cl}_2\text{O}_4$ AND IODOPENTAFLUOROBENZENE

A passivated 30 milliliter cylinder was charged with  $\text{C}_6\text{F}_5\text{I}$  (1.39 millimole) in the dry box. Upon evacuation, freshly purified  $\text{Cl}_2\text{O}_4$  (3.04 millimoles) was condensed into the liquid  $\text{N}_2$ -cooled cylinder. Reaction was obtained by warming the reactor very slowly (through evaporation of a liquid  $\text{N}_2\text{-CO}_2$  slush) to room temperature. After a couple of days at ambient temperature, it was noted that a few milliliters of -196 C noncondensables were present along with 1.72 millimole  $\text{Cl}_2$  (contaminated with a little  $\text{FCIO}_3$ ). No other volatile materials were observed and the nonvolatile shiny, slightly yellow solid product (0.681 grams) corresponded to a 99.6-percent yield of  $\text{C}_6\text{F}_5\text{I} (\text{ClO}_4)_2$ .

#### REACTION OF $\text{Cl}_2\text{O}_4$ AND BROMOPENTAFLUOROBENZENE

Bromopentafluorobenzene (1.31 millimole) was loaded into a 30-milliliter cylinder in the dry box. Subsequently,  $\text{Cl}_2\text{O}_4$  (3.17 millimoles) was added at -196 C from the vacuum line and the reactor was then kept at -45 C for several days. Removal at ambient temperature of all volatile species showed them to be mainly a mixture of  $\text{BrCl}$  and  $\text{Cl}_2$ , which were identified mass spectrometrically together with some unreacted  $\text{Cl}_2\text{O}_4$  and lesser amounts of  $\text{S}_2\text{O}_5\text{F}_2$  (impurity in the  $\text{Cl}_2\text{O}_4$  originally used) and  $\text{Cl}_2\text{O}_7$ . Unreacted  $\text{C}_6\text{F}_5\text{Br}$  or other volatile C-F moieties were not detected. After pumping on the cylinder at ambient temperature for several hours, the remaining product (0.507 grams) was examined in the dry box. An oily, colorless liquid, its infrared spectrum showed C-F bands and very strong covalent  $-\text{ClO}_4$  group bands. Based on the recovered  $\text{BrCl}$ ,  $\text{Cl}_2$ , and  $\text{Cl}_2\text{O}_4$ , the composition of this liquid approaches  $(\text{ClO}_4)_2 \text{C}_6\text{F}_5\text{Cl}$ . The theoretical weight for 1.31 millimole of this product was 0.525 grams.

## REACTION OF $\text{Cl}_2\text{O}_4$ AND SULFURYL CHLORIDE

Chlorine perchlorate (3.87 millimoles) and sulfonyl chloride (1.95 millimole) were reacted at -23 C in a stainless-steel cylinder for several months. At that time it was found that much  $\text{O}_2$  was present which was pumped away without measuring. The -196 ° condensable products were  $\text{Cl}_2$  (3.79 millimoles), a trace of  $\text{ClO}_2$ , and unreacted  $\text{SO}_2\text{Cl}_2$ , which was identified by its infrared spectrum. No  $\text{Cl}_2\text{O}_4$  was recovered.

## FLUORINE FLUOROSULFATE- $\text{CsSF}_5$ REACTION

A sample of  $\text{CsSF}_5/\text{CsF}$  (60:40 millimole percent, 0.40 gram) was reacted with  $\text{FSO}_3\text{F}$  (1.77 millimole) in a 30-milliliter cylinder at ambient temperature for several days. Only a trace of -196 C noncondensable material was observed and the other products were subjected to fractional condensation in a series of cold U-traps. These consisted of unreacted  $\text{FSO}_3\text{F}$  (1.23 millimole) and  $\text{SF}_6$  (0.53 millimole), both identified by their infrared spectra (Ref. 25). Pyrolysis of the solid left in the reactor liberated  $\text{SF}_4$  (0.43 millimole). Thus, of the available  $\text{SF}_5^-$  (0.96 millimole), 55 percent had been converted to  $\text{SF}_6$ . An infrared spectrum of the solid showed only  $\text{CsSO}_3\text{F}$  (Ref. 26).

## CHLORINE FLUOROSULFATE- $\text{CsIF}_4$ REACTION

Solid  $\text{CsIF}_4$  (1.13 millimole) was placed into a 30-milliliter cylinder in the dry box and freshly purified  $\text{ClSO}_3\text{F}$  (1.02 millimole) was added from the vacuum line by condensing at -196 C. The reactants were maintained at -80 C for 48 hours. Re-cooling to -196 C showed no noncondensables had formed. Gradual warming first to -45 C then room temperature while pumping any volatile materials through successive U-traps cooled to -80, -112, and -196 C led to the separation of 0.52 millimole of  $\text{Cl}_2$  and trace amounts of  $\text{S}_2\text{O}_5\text{F}_2$ . These were accompanied by a mixture of  $\text{I}_2/\text{IF}_5$  as shown by appearance and an infrared spectrum. The solid by-product weighed 0.236 gram, which compares well with that calculated (0.277 gram) for 1.02 millimole of  $\text{CsSO}_3\text{F}$  and 0.11 millimole of unreacted  $\text{CsIF}_4$ .

### DIFLUORAMINO FLUOROSULFATE-CsIF<sub>4</sub> REACTION

Cesium tetrafluoroiodine (0.69 millimole) was loaded into a 30-milliliter cylinder in the dry box. After evacuation and cooling the cylinder to -196 C, a sample of NF<sub>2</sub>SO<sub>3</sub>F containing ~20 percent SO<sub>2</sub> (0.69 millimole) was condensed in. Several weeks of reaction at -45 C was followed by workup via fractional condensation of the volatile products at -80, -112, and -196 C. These were unreacted NF<sub>2</sub>SO<sub>3</sub>F (0.23 millimole), SO<sub>2</sub>F<sub>2</sub> (0.46 millimole), and a mixture of I<sub>2</sub>/IF<sub>5</sub>.

### PEROXYDISULFURYL DIFLUORIDE-CsSeF<sub>5</sub> REACTION

After loading CsSeF<sub>5</sub> (3.62 millimoles) into a 30-milliliter cylinder, purified S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> (3.22 millimoles) was condensed in at -196 C and the reaction was allowed to proceed at ambient temperature for a couple of weeks. No -196 C noncondensables were formed and fractional condensation of the gases present was carried out at -45, -95, and -196 C. Unreacted S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> (0.94 millimole) was recovered and SeF<sub>6</sub> (2.30 millimoles). No other volatile material was found. The weight of solid product (1.10 grams) agreed well with that expected (1.12 grams) for a mixture of 2.30 millimoles of CsS<sub>2</sub>O<sub>6</sub>F and 1.32 millimoles of CsSeF<sub>5</sub>.

### PEROXYDISULFURYL DIFLUORIDE-SeF<sub>4</sub> REACTION

A 10-milliliter cylinder was cooled to -196 C and charged with SeF<sub>4</sub> (1.64 millimole) followed by S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> (1.92 millimole). The reactor was warmed slowly to room temperature and left for 1 week.

Vacuum fractionation of the volatile species led to the recovery of unreacted S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> (1.34 millimole) and product SeF<sub>6</sub> (0.55 millimole) as the only gaseous materials. The cylinder contained a white solid (0.260 gram) which was identified as SeF<sub>3</sub><sup>+</sup>SO<sub>3</sub>F<sup>-</sup> by its infrared spectrum (Ref. 17). The yield (1.10 millimole) was 95 percent based on the reacted S<sub>2</sub>O<sub>6</sub>F<sub>2</sub>.

## CHLORINE FLUOROSULFATE-PHOSGENE REACTION

Chlorine fluorosulfate (3.55 millimole) and phosgene (1.84 millimole) were separately condensed into a 30-milliliter cylinder which was held at -196 C. The reactor was warmed to ambient temperature and then heated at 50 C for several hours. The products were separated by fractional condensation at -65, -112, and -196 C. These consisted of  $\text{CO}_2$  and  $\text{Cl}_2$  together with traces of  $\text{COFCl}$  and  $\text{SO}_2\text{F}_2$ , all of which were retained at -196 C. The -112 C fraction was  $\text{S}_2\text{O}_5\text{F}_2$  (1.60 millimole) and the -65 C fraction was  $\text{ClC(O)SO}_3\text{F}$  (0.20 millimole), both of which were identified by their infrared spectra and vapor pressure (Ref. 27 and 28). The yield of  $\text{S}_2\text{O}_5\text{F}_2$  was 90 percent.

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Canoga Park, California 91304

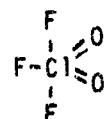
Chlorine Trifluoride Dioxide, ClF<sub>3</sub>O<sub>2</sub>. Synthesis and Properties

by Karl O. Christe\* and Richard D. Wilson

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Abstract

Chlorine trifluoride dioxide was prepared from FNO<sub>2</sub> and ClF<sub>2</sub>O<sub>2</sub><sup>+</sup>PtF<sub>6</sub><sup>-</sup>, the latter being synthesized from FC1O<sub>2</sub> and PtF<sub>6</sub>. Physical properties and the <sup>19</sup>F nmr spectrum are reported. The nmr spectrum suggests the following trigonal bipyramidal structure of symmetry C<sub>2v</sub>



Chlorine trifluoride dioxide forms stable adducts with BF<sub>3</sub> and AsF<sub>5</sub> but not with FNO, FNO<sub>2</sub> or CsF.

Introduction

A brief note on the existence of ClF<sub>3</sub>O<sub>2</sub> has recently been published by Christe<sup>1</sup>. In this paper we report details on its synthesis, purification, and properties. The infrared spectrum of the gas, the solid, and of the matrix isolated species, and the Raman spectrum of the gas and the liquid together with a normal coordinate analysis and computation of thermodynamic properties will be published elsewhere<sup>2</sup>.

Experimental

Materials and Apparatus. The stainless steel-Teflon FEP vacuum system<sup>3</sup>, the glove box, the <sup>19</sup>F nmr spectrometer and sampling technique<sup>4</sup>, and the syntheses and purification of PtF<sub>6</sub>, FC1O<sub>2</sub>, FNO,<sup>3</sup> FNO<sub>2</sub>, BF<sub>3</sub>, and ClF<sub>2</sub>O<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> have previously been described. Cesium fluoride was fused in a platinum crucible and powdered in a dry-box prior to use. All equipment was passivated with ClF<sub>3</sub> and BrF<sub>5</sub> prior to its use.

Purification of ClF<sub>3</sub>O<sub>2</sub>. A sample of ClF<sub>2</sub>O<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> (2.41 mmole), prepared and purified as previously reported<sup>5</sup>, was placed in a passivated Teflon FEP ampoule. Nitryl fluoride (6.83 mmole) was added at -196° and the mixture was kept at -78° for 12 hours with periodic agitation. Volatile products were removed at -78° and separated by fractional condensation through a series of traps kept at -95, -126, and -196°. The -95° trap contained only a very small amount of material which was discarded. The -126° trap contained 2.22 mmole of ClF<sub>3</sub>O<sub>2</sub> which according to its infrared spectrum<sup>2</sup> at 700 mm pressure showed as the only detectable impurity less than 0.1 mole % of FC1O<sub>2</sub>. This sample was used for the subsequent characterization studies. The -196° trap contained the unreacted FNO<sub>2</sub> (4.4 mmole) and a small amount of ClF<sub>3</sub>O<sub>2</sub> (0.2 mmole). The solid residue was shown by its weight and infrared spectrum to be NO<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup>.

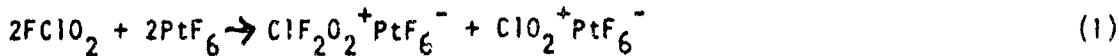
The ClF<sub>3</sub>O<sub>2</sub>-CsF System. Two reactions between ClF<sub>3</sub>O<sub>2</sub> (1.5 mmole) and CsF (1.0 mmole) were carried out in 10 ml stainless steel cylinders at 25° and 105°, respectively. At the lower temperature the cylinder was placed on a mechanical shaker for five days. The volatile material consisted of F<sub>2</sub>, FC1O<sub>2</sub>, and some ClF<sub>3</sub>O<sub>2</sub>. The solid residue had gained 33 mg in weight and was identified by its infrared spectrum<sup>6</sup> as a mixture of Cs<sup>+</sup>ClO<sub>2</sub>F<sub>2</sub><sup>-</sup> and CsF. When the starting materials were heated to 105° for 68 hours, the ClF<sub>3</sub>O<sub>2</sub> had quantitatively decomposed to FC1O<sub>2</sub> and F<sub>2</sub>.

Results and Discussion

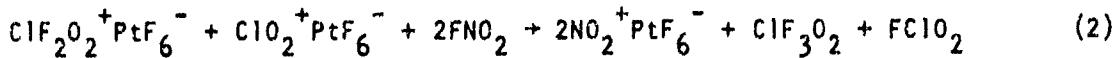
Synthesis. The synthesis of ClF<sub>3</sub>O<sub>2</sub> is best described by the following reaction sequence:

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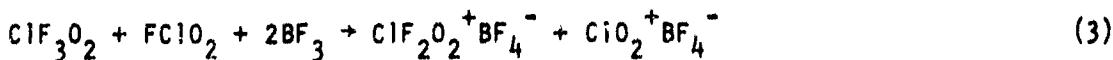
A-2



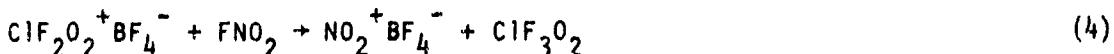
Several side reactions compete with (1) and the yield of  $\text{ClF}_2\text{O}_2^+$  varies greatly with slight changes in the reaction conditions<sup>3</sup>. The  $\text{ClF}_3\text{O}_2$  is then displaced from its  $\text{ClF}_2\text{O}_2^+$  salt according to:



Chloryl fluoride is slightly less volatile than  $\text{ClF}_3\text{O}_2$ . Therefore, most of it can be removed from  $\text{ClF}_3\text{O}_2$  by fractional condensation in a  $-112^\circ$  trap. The remaining  $\text{FCIO}_2$ , however, has to be removed by complexing with  $\text{BF}_3$ :



Since  $\text{ClF}_2\text{O}_2^+\text{BF}_4^-$  is stable<sup>5</sup> at  $20^\circ$  whereas  $\text{ClO}_2^+\text{BF}_4^-$  is not<sup>7</sup>, the latter can be pumped away at  $20^\circ$ . The resulting pure  $\text{ClF}_2\text{O}_2^+\text{BF}_4^-$  is then treated with an excess of  $\text{FNO}_2$  and the evolved  $\text{ClF}_3\text{O}_2$  and unreacted  $\text{FNO}_2$  are readily separated by fractional condensation through a series of  $-126$  and  $-196^\circ$  traps:



Whereas the overall yield of pure  $\text{ClF}_3\text{O}_2$  based on the  $\text{PtF}_6$  used in step 1 was found to be rather low (about 10 mole %), the method was satisfactory to provide enough material to characterize  $\text{ClF}_3\text{O}_2$ . Therefore, no effort was undertaken to search for alternate synthetic routes which might give higher yields of  $\text{ClF}_3\text{O}_2$ .

Properties. Pure  $\text{ClF}_3\text{O}_2$  is colorless as a gas or liquid and white in the solid state. It melts at  $-81.2^\circ$ . Vapor pressures were measured over the range  $-96$  to  $-32^\circ$  and the data for the range  $-64$  to  $-32^\circ$  were fitted by the method of least squares to the equation

$$\log P_{\text{mm}} = 7.719 - \frac{1217.2}{T(\text{°K})} \text{ with an index of correlation of .99998.}$$

The extrapolated boiling point is  $-21.58^{\circ}$ . Measured vapor pressures at the noted temperatures are  $[T(^{\circ}\text{C}), P(\text{mm})]$ :  $-95.64, 7.3$ ;  $-78.73, 25.5$ ;  $-64.34, 77.5$ ;  $-57.69, 117.5$ ;  $-46.32, 226.5$ ;  $-31.93, 470$ . The two lowest temperature points were not used for the computation of the vapor pressure equation because the lowest point was measured for solid  $\text{ClF}_3\text{O}_2$  and the second lowest was too close to the melting point of  $\text{ClF}_3\text{O}_2$ . While at  $-78.73^{\circ}$  the  $\text{ClF}_3\text{O}_2$  sample was all liquid, the observed vapor pressure was reproducibly lower than expected from the above vapor pressure curve. This indicates that close to the melting point some ordering effect occurs in the liquid causing a decrease of the vapor pressure. The latent heat of vaporization of  $\text{ClF}_3\text{O}_2$  is 5.57 kcal/mole and the derived Trouton constant is 22.13, indicating little association in the liquid phase. This is in agreement with the low boiling point and the good agreement between the Raman spectra of the gas and of the liquid<sup>2</sup>. The molecular weight was determined from the vapor density and found to be 127.1 (calcd. for  $\text{ClF}_3\text{O}_2$  124.5). The good agreement indicates little or no association in the gas phase at the pressures used ( $P \sim 1 \text{ atm}$ ).

Chlorine trifluoride dioxide resembles chlorine fluorides and oxyfluorides in its corrosive and oxidizing properties. It appears to be marginally stable in a well passivated system at ambient temperature. It is a strong oxidative fluorinator as evidenced by its tendency to fluorinate metal surfaces to metal fluorides with  $\text{FClO}_2$  formation. It reacts explosively with organic materials and care must be taken to avoid such combinations. The hydrolysis of  $\text{ClF}_3\text{O}_2$  was not quantitatively studied; however, on one occasion a slight leak in an infrared gas cell containing  $\text{ClF}_3\text{O}_2$  resulted in the formation of  $\text{FClO}_3$  and HF indicating the following reaction:



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<sup>19</sup>F nmr Spectrum. The <sup>19</sup>F nmr spectrum of liquid ClF<sub>3</sub>O<sub>2</sub> was measured in the temperature range -20 to -80°. It showed at all temperatures one partially resolved signal centered at -413 ppm below the external standard CFCI<sub>3</sub>. Figure 1 shows the details of the spectrum recorded at -77°. The observed signal is in excellent agreement with an AB<sub>2</sub> pattern<sup>8</sup> with  $\frac{J}{\nu_0\delta} = 1.0$  (for the computed pattern see Figure 1). From these data a value of J<sub>FF</sub> = 443 Hz was calculated. The low chemical shift of -413 ppm for ClF<sub>3</sub>O<sub>2</sub> is in excellent agreement with a heptavalent chlorine fluoride and compares favorably with those observed<sup>4</sup> for ClO<sub>2</sub> (-315 ppm), ClF<sub>6</sub><sup>+</sup> (-388 ppm) and ClF<sub>2</sub>O<sub>2</sub><sup>+</sup> (-310 ppm). The fact that the resonance of the ClF<sub>2</sub>O<sub>2</sub><sup>+</sup> cation was observed upfield from that of ClF<sub>3</sub>O<sub>2</sub> is difficult to rationalize, but seems to be quite general for chlorine fluorides<sup>4</sup>. The fluorine-fluorine coupling constant of 443 Hz observed for ClF<sub>3</sub>O<sub>2</sub> is similar to that of 421 Hz observed for the structurally related ClF<sub>3</sub><sup>4</sup>.

Since the chlorine atom in ClF<sub>3</sub>O<sub>2</sub> does not possess a free valence electron pair, it is pentacoordinated and the ligands should form a trigonal bipyramide. To account for an AB<sub>2</sub> pattern one has to assume two fluorine atoms in either the axial or the equatorial positions:



Of these two models, I has to be preferred for the following four reasons.

(1) The B<sub>2</sub> part of the AB<sub>2</sub> pattern occurs downfield from the A part and in trigonal bipyramidal species the resonance for the axial fluorines occurs at a lower field than that of the equatorial ones<sup>9,10</sup>. (II) In trigonal bipyramidal

molecules the most electronegative ligands generally occupy the axial positions<sup>11</sup>.

(iii) The vibrational spectrum<sup>2</sup> is consistent only with model 1. (iv) In the structurally related  $\text{ClF}_3\text{O}^{12}$  and  $\text{ClF}_3\text{O}^{13}$  molecules (in which the oxygen ligands are replaced by one and two sterically active free electron pairs, respectively) both axial positions are occupied by fluorine atoms.

Adduct Formation. Chlorine trifluoride dioxide forms stable adducts with strong Lewis acids, such as  $\text{BF}_3$ ,  $\text{AsF}_5$ , or  $\text{PtF}_5^5$ . These adducts have ionic structures containing the  $\text{ClF}_2\text{O}_2^+$  cation. A detailed discussion of the vibrational and nmr spectra of this cation will be given elsewhere<sup>5</sup>. The high stability of these adducts can be explained by the change from the energetically unfavorable trigonal bipyramidal structure of  $\text{ClF}_3\text{O}_2$  to the more favorable tetrahedral  $\text{ClF}_2\text{O}_2^+$  configuration<sup>14</sup>. Contrary to  $\text{ClF}_3$ <sup>15</sup> but by analogy with  $\text{ClF}_3\text{O}^{14}$ , it does not form stable adducts with  $\text{FNO}$  or  $\text{FNO}_2$  at temperatures as low as  $-78^\circ$ . This was demonstrated by the various displacement reactions where  $\text{ClF}_3\text{O}_2$  and unreacted  $\text{FNO}$  or  $\text{FNO}_2$  could be readily removed from the reactor at  $-78^\circ$ . With the stronger base,  $\text{CsF}$ , it does not form a stable adduct but decomposes to  $\text{FCIO}_2$  and  $\text{F}_2$  with  $\text{CsF}$  possibly catalyzing the decomposition.

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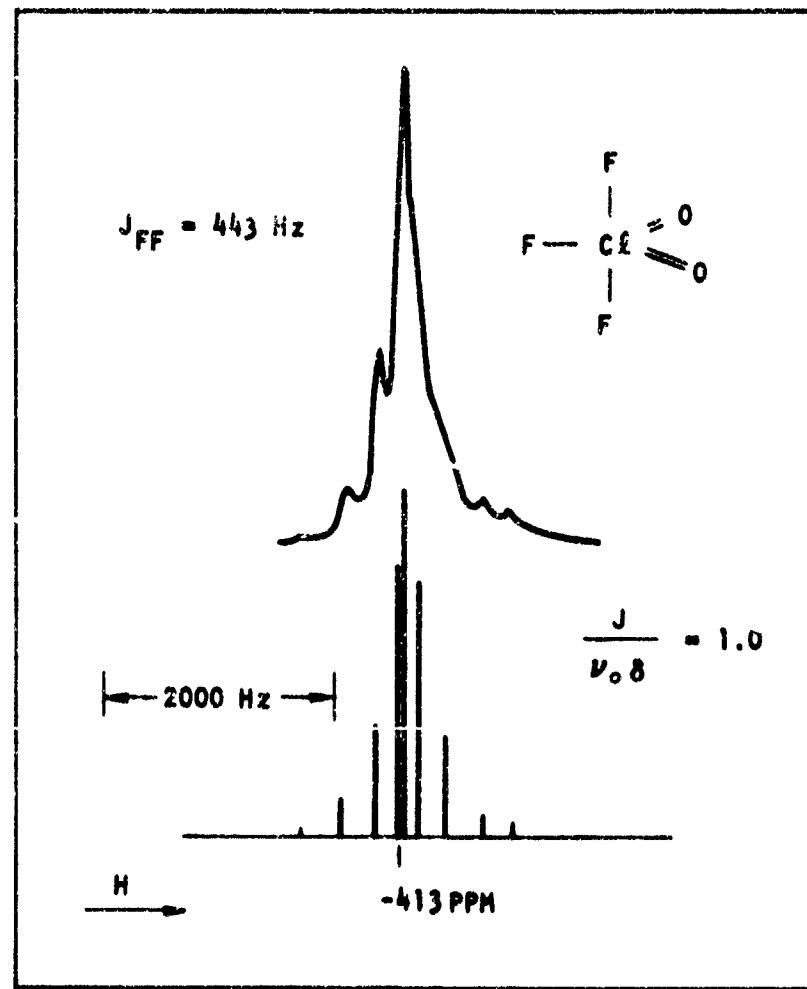
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Diagram Caption

Figure 1.  $^{19}\text{F}$  nmr Spectrum of Liquid  $\text{ClF}_3\text{O}_2$  at  $-77^\circ$  Recorded at 56.4 MHZ.

The Chemical Shift was Measured Relative to the External Standard  
 $\text{CFCl}_3$ .



Contribution from Rocketdyne, A Division of Rockwell International,  
Canoga Park, California 91304

Chlorine Trifluoride Dioxide. Vibrational Spectrum,  
Force Constants, and Thermodynamic Properties

By Karl O. Christe\* and E. C. Curtis

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Abstract

The infrared spectra of gaseous, solid, and matrix isolated  $\text{ClF}_3\text{O}_2$  and the Raman spectra of gaseous and liquid  $\text{ClF}_3\text{O}_2$  are reported. Twelve fundamental vibrations were observed, consistent with a structure of symmetry  $C_{2v}$ . A modified valence force field and thermodynamic properties were computed for  $\text{ClF}_3\text{O}_2$ .

Introduction

A brief note on the existence of  $\text{ClF}_3\text{O}_2$  was recently published by Christe<sup>1</sup>. In a subsequent paper<sup>2</sup>, more details on its synthesis and physical properties were given. Proof for a pseudo-trigonal bipyramidal structure of symmetry  $C_{2v}$  was obtained<sup>2</sup> from its  $^{19}\text{F}$  nmr spectrum, which showed an  $\text{AB}_2$  pattern with strong evidence for the two equivalent fluorine atoms occupying the apical positions. In this paper, we report the complete vibrational spectrum, force constants, and thermodynamic properties of  $\text{ClF}_3\text{O}_2$ .

### Experimental

The synthesis and purification of  $\text{ClF}_3\text{O}_2$  has previously been described<sup>1,2</sup>. The sample used in this investigation showed no detectable impurities except for small amounts of  $\text{FClO}_2$  which easily forms during handling and cannot be separated from  $\text{ClF}_3\text{O}_2$  by fractional condensation<sup>2</sup>. The amount of  $\text{FClO}_2$  formed, however, could be minimized by thorough passivation of the stainless steel-Teflon FEP vacuum system with  $\text{BrF}_5$  and  $\text{ClF}_3$ . For example, the infrared spectrum of gaseous  $\text{ClF}_3\text{O}_2$  at 700 mm pressure showed the presence of less than 0.1 mole percent of  $\text{FClO}_2$ .

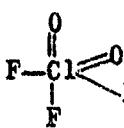
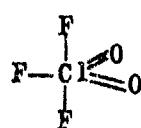
The infrared spectra were recorded on a Perkin Elmer Model 457 spectrophotometer in the range of 4000 to 250  $\text{cm}^{-1}$ . The instrument was calibrated by comparison with standard gas calibration points<sup>3</sup>. The gas cell was made of Teflon and had a path length of 5 cm and AgCl windows. The apparatus, materials, and technique used for the matrix isolation study have previously been described<sup>4,5</sup>. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å line of an Ar-ion laser as the exciting line. A stainless steel cell with Teflon O-rings and sapphire windows was used for obtaining the spectrum of the gas. The design of this cell was similar to that of a cell described previously<sup>6</sup>. The spectrum of the liquid was obtained using a Teflon FEP capillary as the sample container in the transverse excitation transverse viewing mode.

### Results and Discussion

Vibrational Spectra. Figure 1 shows the infrared spectra of gaseous, solid, and  $\text{N}_2$ -matrix isolated  $\text{ClF}_3\text{O}_2$  and the Raman spectra of gaseous and liquid  $\text{ClF}_3\text{O}_2$  at various concentrations. The spectra of solid  $\text{ClF}_3\text{O}_2$  were corrected for small amounts of  $\text{FClO}_2$ . The  $\text{FClO}_2$  bands were verified by depositing pure  $\text{FClO}_2$  on top

of the  $\text{ClF}_3\text{O}_2$  sample and observing the relative growth rates of the bands. Figure 2 shows the most intense infrared bands of gaseous and matrix isolated  $\text{ClF}_3\text{O}_2$  at higher resolution allowing some conclusions about the band contours and the determination of the  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic shifts. Table I lists the observed frequencies. Table II lists the fundamental vibrations of  $\text{ClF}_3\text{O}_2$  and their assignment compared to those of the related species,  $\text{ClF}_3$ ,  $\text{ClF}_3\text{O}$ ,  $\text{ClF}_2\text{O}_2$ <sup>7</sup>,  $\text{ClF}_4$ <sup>8</sup>,  $\text{ClF}_4^+$ <sup>9</sup>, and  $\text{ClO}_2^+$ <sup>10</sup>.

The structure of  $\text{ClF}_3\text{O}_2$  can be derived from a trigonal bipyramidal, in which the two oxygen ligands could occupy either both apical (I), or one apical and one equatorial (II), or two equatorial (III) positions. These three models belong to different point groups and should differ markedly in their

			
	<u>I</u>	<u>II</u>	<u>III</u>
Point Group	$D_{3h}$	$C_s$	$C_{2v}$
Total Number of Fundamentals	8	12	12
Infrared Active	5	12	11
Raman Active	6	12	12
Polarized Raman Bands	2	8	5

vibrational spectra. The observation of a total of 12 fundamentals for  $\text{ClF}_3\text{O}_2$  (see Figures 1 and 2 and Table I) with a minimum of ten bands being active in the infrared and the Raman spectrum, together with the occurrence of four or five

TABLE I

Vibrational Spectra of  $\text{ClF}_3\text{O}_2$  and their Assignment in Point Group  $\text{C}_{2v}$ 

Observed Frequencies ( $\text{cm}^{-1}$ ), Intensities <sup>a</sup>				Assignment	
Gas	Infrared		Raman		
	Solid	Gas	Gas	Liquid	
	Matrix Isolated	Neat			
2655 vw					$2 \times 1327 = 2654$
2415 vw	2420 2405 2385	vw	2405 vw		$1093 + 1327 = 2420$
2184 vw			2180 vw		$2 \times 1093 = 2186$
2012 vw	2012 vw		2010 vw		$683 + 1327 = 2010$
1860 vw			1850 vw		$520 + 1327 = 1847$
1776 vw					$\begin{cases} 1093 + 695 = 1788 \\ 1093 + 683 = 1776 \end{cases}$
1625 vw					$1093 + 531 = 1624$
1615 vw		1610 vw			$\begin{cases} 1093 + 520 = 1613 \\ 286 + 1327 = 1613 \end{cases}$
1579 vw					$1093 + 487 = 1580$
1499 vw		1495 vw			$\begin{cases} 2 \times 487 + 520 = 1494 \\ 683 + 286 + 531 = 1500 \end{cases}$
1375 vw		1375 vw			$683 + 695 = 1378$
1368 vw	1365 vw				$2 \times 683 = 1366$
1341					
1331	1331.4 s	1327 s			$\nu_{10}^{35}\text{Cl} (B_2)$
1317	vs	1318.8 ms	1315 m, sh	1320 (0.1), br	$1093 + 222 = 1315$
1306		1307.8 ms	1305 m, sh		$\nu_{10}^{37}\text{Cl} (B_2)$
1230 vw	1230 vw				$520 + 695 = 1215$
1218 vw	1218 vw				$683 + 531 = 1214$
1207 vw		1200 vw			$683 + 520 = 1203$
					$\nu_2 + \nu_3 (A_1)$

TABLE I (continued)

Vibrational Spectra of  $\text{ClF}_3\text{O}_2$  and their Assignment in Point Group  $\text{C}_{2v}$ 

Observed Frequencies ( $\text{cm}^{-1}$ ), Intensities <sup>a</sup>				Assignment		
Gas	Infrared		Raman		Assignment	
	Solid		Gas	Liquid		
	Matrix Isolated	Neat				
1195 vw	1203 vw			$2 \times 592 = 1184$	$v_8 (\text{A}_1)$	
1186 vw		1150 vw		$487 + 691 = 1182$	$v_4 + v_7 (\text{B}_1)$	
1174 vw	1173 1169 vw			$683 + 487 = 1170$	$v_2 + v_4 (\text{A}_1)$	
		1116 vw		$417 + 693 = 1112$	$v_6 + v_7 (\text{B}_2)$	
				$520 + 592 = 1112$	$v_3 + v_8 (\text{B}_1)$	
1093 s	1093 ms		1093(3.5)	$1090(4.1)$	$v_1^{35}\text{Cl} (\text{A}_1)$	
	1086 m			pol <sup>b</sup>	$v_1^{37}\text{Cl} (\text{A}_1)$	
1080 vw						
1073 vw		1070 vw, sh		$695 + 372 = 1067$	$v_7 + v_9 (\text{A}_1)$	
1065 vw				$2 \times 531 = 1062$	$2 v_{11} (\text{A}_1)$	
985 vw				$286 + 695 = 981$	$v_5 + v_7 (\text{B}_1)$	
978 vw	974 vw	968 vw		$2 \times 487 = 974$	$2 v_4 (\text{A}_1)$	
881 vw				$286 + 592 = 878$	$v_5 + v_8 (\text{B}_1)$	
856 vw				$487 + 372 = 859$	$v_4 + v_9 (\text{B}_1)$	
805 vw		810 vw	806 vw	$520 + 286 = 806$	$v_3 + v_5 (\text{A}_1)$	
797 vw						
786 vw				$417 + 372 = 789$	$v_6 + v_9 (\text{B}_2)$	
772 vw		760 sh, vw		$487 + 286 = 773$	$v_4 + v_8 (\text{A}_1)$	
758 vw				$531 + 222 = 753$	$v_{11} + v_{12} (\text{A}_1)$	

TABLE I (continued)

Vibrational Spectra of  $\text{ClF}_3\text{O}_2$  and their Assignment in Point Group  $\text{C}_{2v}$ 

Gas	Observed Frequencies ( $\text{cm}^{-1}$ ), Intensities <sup>a</sup>			Assignment	
	Infrared		Raman		
	Solid	Gas	Gas	Liquid	
702					
695	686.3 vs	655 vs, br			$\nu_7$ $^{35}\text{Cl}$ ( $\text{B}_1$ )
687 sh vs	682.6 m	700 sh,s	683(10)	675(6.5) pol	$\nu_7$ $^{35}\text{Cl}$ ( $\text{B}_1$ )
683	674.7 s				$\nu_2$ $^{35}\text{Cl}$ ( $\text{A}_1$ )
679 sh					$\nu_2$ $^{35}\text{Cl}$ ( $\text{A}_1$ )
593 s	591 ms	570 s		586(0.1)	$\nu_8$ ( $\text{B}_1$ )
543	531 m				$\nu_{11}$ $^{35}\text{Cl}$ ( $\text{B}_2$ )
531	528 mw	527 m	540 sh	530 sh	$\nu_{11}$ $^{37}\text{Cl}$ ( $\text{B}_2$ )
520 sh,mw	519 w	520 sh,w	520(7.5)	518(10) pol	$\nu_3$ ( $\text{A}_1$ )
	487 vw	473 mw	487(6.1)	481(9.0) pol	$\nu_4$ ( $\text{A}_1$ )
	417 vw	417 vw		402 (0+)	$\nu_6$ ( $\text{A}_2$ )
	372 w	368 w			$\nu_9$ ( $\text{B}_1$ )
	287 w	290 w	285(0.9)	285(1.6)	$\nu_8$ ( $\text{A}_1$ )
			222(0.7)	222(1.2)	$\nu_{12}$ ( $\text{B}_2$ )

(a) Uncorrected Raman intensities representing the relative peak height, the relative peak widths, and hence, the relative peak heights change from gaseous to liquid  $\text{ClF}_3\text{O}_2$ .

(b) Only qualitative polarization measurements could be obtained, owing to the optical activity of the sapphire windows of the gas cell and owing to the tendency of  $\text{ClF}_3\text{O}_2$  to act as a plasticizer for the Teflon FEP capillaries.

TABLE II  
Vibrational Spectrum of  $\text{ClF}_3\text{O}_2$  Compared to Those of Similar Molecules and Ions

Wavenumber (cm <sup>-1</sup> )	Assignment of Mode <sup>a</sup>	Observed Frequencies (cm <sup>-1</sup> ), Intensities:										Assignment for $\text{ClF}_3\text{O}_2$ in Point Group $\text{C}_2v$
		$\text{Cl}-\text{O}_2$	$\text{O}_2-\text{Cl}$	$\text{Cl}-\text{O}_2-\text{Cl}$	$\text{O}_2-\text{Cl}-\text{O}_2$	$\text{Cl}-\text{O}_2-\text{Cl}$	$\text{O}_2-\text{Cl}-\text{O}_2$	$\text{Cl}-\text{O}_2-\text{Cl}$	$\text{O}_2-\text{Cl}-\text{O}_2$	$\text{Cl}-\text{O}_2-\text{Cl}$	$\text{O}_2-\text{Cl}-\text{O}_2$	
1063 s	1063(4)p	1222	IR	IR	IR	IR	IR	IR	IR	IR	IR	1044 s
662 s	663(10)p	666 s	664(2.4)i	752 s	752 s,p	830 - 816	—	1075(10)	1044(10)	$A_1$	$\nu_1$	sp. $\text{ClO}_2$ stretch
515 w	520(8)p	—	—	—	—	—	—	558(1.2)	521 s	$\nu_2$	$\text{ClF}_3\text{O}_2$ stretch	
487 vw	487(6)p	473 vw	462(1.0)p	540 w	529 v,p	566 w	567(7)	542(1.2)	363(19)	$\nu_3$	$\text{ClO}_2$ sciss.	
267 w	265(1)	c, w	224(0.5)i	325 s	320 v,p	c	327(1)	c	166(6.7)	$\nu_4$	sp. $\text{F}_2\text{ClO}_2$ stretch	
(417) <sup>b</sup>	412(w)	412 w	414(0.2)i,p	—	—	474(1)	466(1)	—	—	$\nu_5$	$\text{F}_2\text{ClO}_2$ sciss. in $\text{ClO}_3$ plane	
636 vs	632 vs	632 vs	702 vs	770 vs	—	510 vs	—	—	—	$\nu_6$	tert. sciss.	
362 s	358(w)	359 w	400(1)	—	538 w	536(2)	530(2)	337(1)	—	$\nu_7$	antist. $\text{F}_2\text{ClO}_2$ stretch	
372 w	—	442 w	431 w,p	—	—	—	—	—	—	$\nu_8$	$\text{ClO}_2$ wagging	
1227 <sup>b</sup> vs	1229(w)	1229	—	—	—	1135 vs	1221(0.8)	1230 vs	1234(1)	$\nu_9$	Antist. $\text{F}_2\text{ClO}_2$ stretch in $\text{ClO}_3$ plane	
121 s	120(1)	120 w	316(0.1)	328 s	322 w	326 w	326(6w)	370 w	376(6)	$\nu_{10}$	Antist. $\text{ClO}_2$ stretch	
c	222(1)	—	—	—	—	—	—	—	—	$\nu_{11}$	$\text{F}_2\text{ClO}_2$ sciss. out of $\text{ClO}_3$ plane	
									—	$\nu_{12}$		

(a) Observed only for solid  $\text{ClF}_3\text{O}_2$ .

(b) Frequency corrected for disturbance by Fermi resonance.

(c) Below frequency range of spectrometer used.

(d) K. O. Christe and R. C. Curris, *Inorg. Chem.*, **11**, 2166 (1972).

(e) According to the potential energy distribution, the 224 and 320  $\text{cm}^{-1}$  modes are an almost equal mixture of the corresponding symmetry coordinates and, hence, are very characteristic

(f) H. Seig, H. H. Claassen, and J. H. Hollency, *J. Chem. Phys.*, **52**, 3517 (1970).

(g) K. O. Christe and W. Seewald, to be published.

(h) K. O. Christe and R. C. Curris, *Inorg. Chem.*, **11**, 35 (1972).

(i) K. O. Christe, C. J. Szwed, B. Filipovich, and W. Seewald, *Inorg. Chem.*, **2**, 349 (1983).

(j) The modes in the  $\text{ClO}_3$  dodecahedron are highly mixed (see PD, Table VI) and, therefore, difficult to associate with the frequencies.

polarized Raman bands rule out point group  $D_{3h}$  and favor  $C_{2v}$  over  $C_s$ . Additional strong evidence for symmetry  $C_{2v}$  consists of the relative infrared and Raman intensities and of the frequency separation of the  $\text{ClF}_2$  stretching modes, indicating a highly symmetric, i.e., approximately linear,  $\text{FClF}$  arrangement. Comparison with the vibrational spectra of a number of related species having geometries similar to that of model III (see Table II) also supports model III. This conclusion in favor of model III, reached exclusively on the basis of the observed vibrational spectrum, is in excellent agreement with the observed  $^{19}\text{F}$  nmr spectrum<sup>2</sup> and the general observation<sup>12</sup> that in trigonal bipyramidal molecules, the most electro-negative ligands always occupy the apical positions.

The 12 fundamentals expected for an  $\text{XY}_3\text{Z}_2$  molecule of symmetry  $C_{2v}$  are classified as  $5A_1 + A_2 + 3B_1 + 3B_2$ . All of these should be active in both the infrared and Raman spectrum except for the  $A_2$  mode which should be only Raman active. The strong bands at about 1327 and  $1093\text{ cm}^{-1}$  have frequencies too high for any  $\text{Cl-F}$  stretching modes and, hence, must be assigned to the antisymmetric and symmetric  $\text{ClO}_2$  stretching modes, respectively. The antisymmetric axial  $\text{F-Cl-F}$  stretching mode should occur in the  $600-800\text{ cm}^{-1}$  frequency range, be of very high infrared and very low Raman intensity, and by comparison with  $\text{ClF}_3\text{O}$ <sup>8</sup> and  $\text{ClF}_3$ <sup>7</sup> show a  $^{35}\text{Cl}-^{37}\text{Cl}$  isotopic shift of about  $11\text{ cm}^{-1}$ . Consequently, this mode must be assigned to the bands observed at 686.3 and  $674.7\text{ cm}^{-1}$  in the  $\text{N}_2$  matrix. The symmetric axial  $\text{F-Cl-F}$  stretching mode should occur in the  $450 - 570\text{ cm}^{-1}$  frequency range and be of high intensity in the Raman and of very low intensity in the infrared spectrum. There are two intense polarized Raman bands at 520 and  $487\text{ cm}^{-1}$ , respectively, which might be assigned to this mode. Since the  $487\text{ cm}^{-1}$  band is of much lower infrared intensity (for an ideal linear, symmetric  $\text{F-Cl-F}$  group,

this mode should be infrared inactive and indeed was not observed for gaseous  $\text{ClF}_3\text{O}_2$ ), it is assigned to the symmetric axial FClF stretching mode. The fifth stretching mode involving the equatorial fluorine is expected to occur between 650 and  $800 \text{ cm}^{-1}$ , to be of medium to strong infrared intensity, and to give rise to an intense polarized Raman line. Clearly this mode must be assigned to the  $682.8 \text{ cm}^{-1}$  band in the matrix and the  $683 \text{ cm}^{-1}$  Raman band. Comparison with  $\text{ClF}_3$  and  $\text{ClF}_3^7$  indicates a  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic shift of about  $7 \text{ cm}^{-1}$  for this mode. Its  $^{37}\text{Cl}$  part could not directly be observed for the matrix isolated sample owing to its accidental coincidence with the much more intense  $^{37}\text{Cl}$  antisymmetric FClF stretching mode.

The remaining seven bands must be assigned to the deformation modes. Of these, only the  $A_2$  torsion mode ideally should be infrared inactive. Since the Raman band at about  $410 \text{ cm}^{-1}$  shows no counterpart in the infrared spectrum of the gas, it is assigned to this torsion mode. The  $520 \text{ cm}^{-1}$  Raman band is clearly polarized and, hence, must belong to species  $A_1$ . Based on its relatively high frequency, it must represent the  $\text{ClO}_2$  scissoring mode and not the axial F-Cl-F deformation. Based on the observed Fermi resonance (see below) between the  $1327 \text{ cm}^{-1}$  band and the  $1093 + 222$  combination band, the  $222$  and  $1327 \text{ cm}^{-1}$  bands must belong to the same symmetry species. Consequently, the  $222 \text{ cm}^{-1}$  band must represent the  $B_2$  axial F-Cl-F deformation. There are four bands occurring at about  $590$ ,  $530$ ,  $370$ , and  $290 \text{ cm}^{-1}$ , respectively, left for assignment. Two of these represent a rocking and wagging motion, respectively, of the  $\text{ClO}_2$  group and, therefore, should have higher frequencies than the two remaining FClF deformations. Assignment of the  $591 \text{ cm}^{-1}$  band to the  $\text{ClO}_2$  wag and of the  $531 \text{ cm}^{-1}$  band to the  $\text{ClO}_2$  rock can be made based on the observed gas phase band contours and the observed  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic splittings (see Figure 2, traces G to K). The  $591 \text{ cm}^{-1}$  band shows a Q-R

branch splitting for  $^{35}\text{ClF}_3\text{O}_2$  of about  $8 \text{ cm}^{-1}$  comparable to that observed for the antisymmetric FClF stretch,  $\nu_7$  ( $B_1$ ). The  $531 \text{ cm}^{-1}$  band exhibits a missing Q branch and a P-R branch separation of about  $11 \text{ cm}^{-1}$  comparable to that observed for the antisymmetric  $\text{ClO}_2$  stretch,  $\nu_{10}$  ( $B_2$ ). Furthermore, the  $531 \text{ cm}^{-1}$  band shows a larger  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic splitting than the one at  $591 \text{ cm}^{-1}$  in agreement with the values (see Table IV) computed for the  $\text{ClO}_2$  rocking and wagging motions, respectively. The remaining two bands at  $286$  and  $372 \text{ cm}^{-1}$  are assigned to the axial F-Cl-F scissoring mode  $\nu_5$  ( $A_1$ ) and the antisymmetric in plane  $\text{ClF}_3$  deformation mode,  $\nu_9$  ( $B_1$ ), respectively. This assignment is based on the observed frequencies and the relative infrared and Raman intensities. The assignment of the  $286 \text{ cm}^{-1}$  Raman band to an  $A_1$  mode is further supported by the fact that it appears to be weakly polarized. The excellent fit between all the observed and computed combination bands and overtones (see Table I) without violation of the selection rules ( $B_1 + B_2 = A_2$  and  $A_1 + A_2 = A_2$  combinations are infrared forbidden) also suggests the correctness of the above assignments.

The observation of three relatively intense bands in the  $\text{N}_2$  matrix for the antisymmetric  $\text{ClO}_2$  stretching mode,  $\nu_{10}$  ( $B_2$ ), requires further explanation. For this mode, a  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic splitting of about  $15 \text{ cm}^{-1}$  might be predicted by comparison with that observed for related  $\text{ClO}_2^+ + \text{H}_2$ . The combination band,  $1093 + 222 = 1315 \text{ cm}^{-1}$ , should show a considerably smaller  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic splitting of about  $8 \text{ cm}^{-1}$  (see Table IV) and based on its frequency fall between the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopic bands of  $\nu_{10}$ . As shown schematically in Figure 2, Fermi resonance between  $\nu_{10}$  and  $\nu_1 + \nu_{12}$  will increase the frequency separation between the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  components of  $\nu_{10}$  and decrease that between the two isotopic combination bands. This assignment is supported by the observed bandwidths at half height which are similar ( $\sim 2.0 \text{ cm}^{-1}$ ) for the  $1331.4$  and  $1307.8 \text{ cm}^{-1}$  bands,

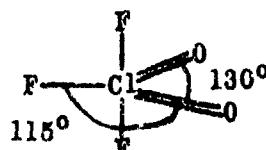
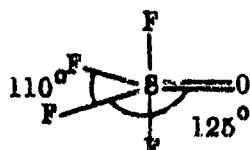
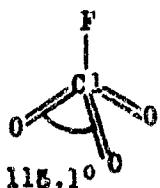
but larger ( $\sim 3.0 \text{ cm}^{-1}$ ) for the  $1318.8 \text{ cm}^{-1}$  band. The disturbance by Fermi resonance can also account for the strongly increased intensity of the combination band. The fact that the frequency of the  $1318.3 \text{ cm}^{-1}$  band is closer to  $1307.8 \text{ cm}^{-1}$  than to  $1331.4 \text{ cm}^{-1}$ , agrees with the observed relative intensities. The  $1307.8 \text{ cm}^{-1}$  band has lost relatively more of its original intensity as demonstrated by the observed intensity ratio of 1:4.4 for the  $1307.8$  and  $1331.4 \text{ cm}^{-1}$  bands. For undisturbed  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic species, this ratio should be 1:3.07.

The observed gas phase infrared band contours are complicated by the  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic splittings, Fermi resonance, and two double coincidences of  $\nu_7$  with  $\nu_2$  and of  $\nu_{11}$  with  $\nu_3$ , respectively. However, for most of the bands, the R branches of the  $^{35}\text{Cl}$  isotope are well separated (see Figure 2). Since the geometry of  $\text{ClF}_3\text{O}_2$  of symmetry  $C_{2v}$  can be estimated (see below), the three principal moments of inertia were computed resulting in  $A = 0.150$ ,  $B = 0.106$ , and  $C = 0.095 \text{ cm}^{-1}$ . Based on these values, the infrared band contours were estimated for  $\text{ClF}_3\text{O}_2$ , according to the method of Ueda and Shimaouchi<sup>13</sup>. Using No. 33 of Ueda's Figure 3,<sup>13</sup> one should expect for the  $B_1$  modes an A-type band contour with a sharp Q branch and a P-R branch separation of about  $16 \text{ cm}^{-1}$ . As can be seen from Figure 2, the  $686$  and  $591 \text{ cm}^{-1}$  bands show the predicted band shape and branch separation and, therefore, may be assigned with confidence to  $\nu_7$  and  $\nu_8$ , respectively. The  $1331$  and  $531$  bands do not show a Q branch as expected for B-type bands of species  $B_2$ . Consequently, the observed band contours are consistent with the proposed structure of symmetry  $C_{2v}$  and the assignments listed in Table I.

Comparison between the vibrational spectrum of  $\text{ClF}_3\text{O}_2$  and those of related species (Table II) shows good agreement and strongly supports the above assignments for  $\text{ClF}_3\text{O}_2$ . Two features in the  $\text{ClF}_3\text{O}_2$  spectrum, however, require further comment. The  $\text{ClO}_2$  stretching mode,  $\nu_3 (A_1)$ , is unexpectedly intense in the Raman

spectrum. Since the frequency of  $\nu_3$  is close to that of the intense  $\nu_2$  ( $A_1$ ) mode and since these motions could easily couple (as indicated by the normal coordinate transformation  $L^{-1}$  and to some extent by the PFD), this represents a plausible explanation for its high intensity. Alternate explanations, such as Fermi resonance between the symmetric axial  $\text{FClF}$  stretching mode  $\nu_4$  and  $222 + 286 = 508$  can be ruled out because they belong to different symmetry species. Resonance between  $\nu_3$  and  $\nu_4$  can also be eliminated because the observed combination bands involving either  $\nu_3$  or  $\nu_4$  show a good frequency fit, indicating that the fundamentals are undisturbed. Secondly, the frequencies of the two axial  $\text{FClF}$  scissoring modes (in and out of the  $\text{ClF}_3$  plane, respectively) are strongly influenced by the point group of the corresponding molecules and by the presence or absence of other modes in the same symmetry species and, hence, are difficult to correlate. Furthermore, in  $\text{ClF}_3\text{O}$ , these two frequencies are not characteristic and are an almost equal mixture of the corresponding symmetry coordinates.<sup>8</sup>

Force Constants. The potential and kinetic energy metrics for  $\text{ClF}_3\text{O}_2$  were computed by a machine method<sup>14</sup>. The geometry assumed for this computation was  $D(\text{ClO}) = 1.40 \text{ \AA}$ ,  $R(\text{ClF}_{\text{eq}}) = 1.62 \text{ \AA}$ ,  $\nu(\text{ClF}_{\text{ax}}) = 1.72 \text{ \AA}$ ,  $\alpha(\text{OClO}) = 130^\circ$ ,  $\beta(\text{F}_{\text{eq}}\text{ClF}_{\text{ax}}) = \delta(\text{OClF}_{\text{ax}}) = 90^\circ$ , and  $\gamma(\text{OClF}_{\text{eq}}) = 115^\circ$ , based on the observed geometries of  $\text{ClF}_3$ <sup>15</sup> and  $\text{FClO}_3$ <sup>16</sup> and a correlation<sup>17</sup> between ClO bond length and stretching frequency. The deviation of the OClO band angle from the ideal  $120^\circ$  was estimated by comparison with the known geometries of  $\text{SF}_4\text{O}$ <sup>18</sup> and  $\text{FClO}_3$ <sup>16</sup>.



R-9262

B-12

The symmetry coordinates used for  $\text{ClF}_3\text{O}_2$  are given in Table III. The bending coordinates were weighted by unit (1 Å) distance so the stretching force constants have units of mdyn/Å, the deformation force constants units of mdynÅ/radian<sup>2</sup>, and the stretch-bend interaction constants mdyn/radian. The G matrix and Z transformation were found numerically by the computer and, hence, are not given here.

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. Owing to the underdetermined nature (28 symmetry force constants and 12 frequencies) of the problem a diagonal force field was computed assuming all off-diagonal symmetry force constants equal to zero. In the  $A_1$  and  $B_1$  block, however, non-zero values were required for several off-diagonal constants to be able to reproduce the observed frequencies. The quality of the resulting force field was examined by comparing the computed  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic shifts with those observed. The observed Cl isotopic shifts were then used to improve the force field by introducing off-diagonal constants until the calculated isotopic shifts agreed with the observed ones. Those interaction constants not significantly influencing the isotopic shift were not changed while those introduced were required to achieve a fit between observed and computed isotopic shifts. The force field is still not unique and other solutions are certainly possible. Species  $A_1$  contains 15 symmetry force constants. Of these, three off diagonal terms, i.e.  $F_{14}$ ,  $F_{24}$ , and  $F_{34}$ , may be neglected<sup>19</sup> since their corresponding G matrix elements are zero. Therefore, eight frequencies ( $5\ 35\text{Cl} + 3\ 37\text{Cl}$ ) are available for obtaining 12 symmetry force constants. In species  $Z_1$  and  $B_2$  5 frequency values are available for obtaining six symmetry force constants. Numerical experiments indicated that plausible force fields and PED values

TABLE III  
Symmetry Coordinates<sup>a</sup> for ClF<sub>3</sub>O<sub>2</sub>

A <sub>1</sub>	s <sub>1</sub>	$1/\sqrt{2} (\Delta D_1 + \Delta D_2)$
	s <sub>2</sub>	$\Delta R$
	s <sub>3</sub>	$1/\sqrt{6} (2\Delta\alpha - \Delta\gamma_1 - \Delta\gamma_2)$
	s <sub>4</sub>	$1/\sqrt{2} (\Delta r_1 + \Delta r_2)$
	s <sub>5</sub>	$1/\sqrt{12} (2\Delta\beta_1 + 2\Delta\beta_2 - \Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$
	s <sub>r1</sub>	$1/\sqrt{3} (\Delta\alpha - \Delta\gamma_1 + \Delta\gamma_2) = 0$
	s <sub>r2</sub>	$1/\sqrt{6} (\Delta\beta_1 + \Delta\beta_2 + \Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4) = 0$
A <sub>2</sub>	s <sub>6</sub>	$1/\sqrt{4} (\Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 + \Delta\delta_4)$
B <sub>1</sub>	s <sub>7</sub>	$1/\sqrt{2} (\Delta r_1 - \Delta r_2)$
	s <sub>8</sub>	$1/\sqrt{4} (\Delta\delta_1 - \Delta\delta_2 + \Delta\delta_3 - \Delta\delta_4)$
	s <sub>9</sub>	$1/\sqrt{2} (\Delta\beta_1 - \Delta\beta_2)$
B <sub>2</sub>	s <sub>10</sub>	$1/\sqrt{2} (\Delta D_1 - \Delta D_2)$
	s <sub>11</sub>	$1/\sqrt{2} (\Delta\gamma_1 - \Delta\gamma_2)$
	s <sub>12</sub>	$1/\sqrt{4} (\Delta\delta_1 + \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$

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(a) s<sub>r1</sub> and s<sub>r2</sub> are the redundant coordinates and  $\delta_1 = \frac{1}{2}O_1ClF_2$ ,  
 $\delta_2 = \frac{1}{2}O_1ClF_3$ ,  $\delta_3 = \frac{1}{2}O_2ClF_2$ , and  $\delta_4 = \frac{1}{2}O_2ClF_3$ .

TABLE IV

Observed Frequencies (cm<sup>-1</sup>), Symmetry Force Constants<sup>a</sup>, and Computed and Observed <sup>35</sup>Cl and <sup>37</sup>Cl Isotopic Shifts (cm<sup>-1</sup>)

				<u>Δν Comp.</u>	<u>Δν Obsd.</u>
<b>A<sub>1</sub></b>	$\nu_1$	1093	$F_{11} = f_D + f_{DD}$	= 9.14	7.1
			$F_{13} = 1/\sqrt{3} (2f_{D\alpha} - f_{D\gamma} - f_{D\gamma'})$	= 0.70	7.2
	$\nu_2$	683	$F_{22} = f_R$	= 3.35	6.8
			$F_{23} = \sqrt{2/3} (f_{R\alpha} - f_{R\gamma})$	= -0.30	~7
	$\nu_3$	520	$F_{33} = 1/3 (2f_\alpha + f_\gamma + f_\gamma' - 4f_{\alpha\gamma})$	= 1.27	0.8
	$\nu_4$	487	$F_{44} = f_r + f_{rr}$	= 2.65	0
	$\nu_5$	286	$F_{55} = 1/3 (2f_\beta + f_\delta + 2f_{\beta\delta} + f_{\delta\delta} + f_{\delta\delta'} + f_{\delta\delta''} - 4f_{\beta\delta} - 4f_{\beta\delta'})$	= 1.37	0.5
<b>R-9262</b>	$\nu_6$	417	$F_{66} = f_6 - f_{66} - f_{66'} + f_{66''}$	= 1.13	0
<b>B<sub>1</sub></b>	$\nu_7$	695	$F_{77} = f_r - f_{rr}$	= 2.75	11.7
			$F_{78} = \sqrt{2} (f_{r\delta} - f_{r\delta'})$	= 0.70	11.6
			$F_{79} = f_{r\beta} - f_{r\beta'}$	= 0.20	
	$\nu_8$	592	$F_{88} = f_\delta - f_{66} + f_{66'} - f_{66''}$	= 2.15	0
			$F_{89} = \sqrt{2} (f_{\beta\delta} - f_{\beta\delta'})$	= -0.44	
	$\nu_9$	372	$F_{99} = f_\beta = f_{\beta\beta}$	= 1.31	1.0
<b>B<sub>2</sub></b>	$\nu_{10}$	1327	$F_{10,10} = f_{\gamma\gamma} - f_{DD}$	= 9.33	16.8
	$\nu_{11}$	531	$F_{11,11} = f_{\gamma\gamma} - f_{\gamma\gamma'}$	= 1.63	2.2
	$\nu_{12}$	222	$F_{12,12} = f_{\gamma\gamma} + f_{\delta\delta} - f_{\delta\delta'} - f_{\delta\delta''}$	= 0.78	0.6
<i>Δν</i>					
					<i>Δν</i> constants in mdyn/k. deformation constants in mdyn/radian <sup>2</sup> , and stretch-bend interaction constants in

could be achieved only with values reasonably close to those shown in Table IV. The requirement of a large off-diagonal constant for  $B_1$  has previously also been found for the structurally related pseudo-trigonal bipyramidal  $SF_4O$  molecule<sup>20</sup>.

The internal coordinate stretching force constants can be computed; however, the bending valence force constants cannot be completely separated from the interaction constants without making additional simplifying assumptions (see Table V). The constants of greatest interest are the stretching force constants since they are a measure of the strength of the various bonds. Uncertainty estimates are difficult to make owing to the underdetermined nature of the force field. The value of the  $Cl=O$  stretching force constant should have the smallest uncertainty (0.1 mdyn/Å or less) owing to the highly characteristic nature of the  $ClO_2$  stretching modes and the use of isotopic shifts for its computation. Its value of 9.23 mdyn/Å is in excellent agreement with that of 9.37 mdyn/Å found for  $ClF_3O$ <sup>8</sup> and the General Valence Force Field values of 9.07 and 8.96 mdyn/Å reported for  $FClO_2$ <sup>21</sup> and  $ClO_2^+$ <sup>11</sup>, respectively. The values of the  $ClF$  stretching force constants are comparable to those previously reported for the related pseudo-trigonal bipyramidal molecules,  $ClF_3$ <sup>22</sup> and  $ClF_3O$ <sup>8</sup> (see Table V). In all three molecules, the stretching force constant of the equatorial  $ClF$  bond is significantly higher than that of the two axial bonds, although their relative difference decreases with increasing oxidation state of the central atom. The difference in bond strength between equatorial and axial bonds implies significant contributions from semi-ionic three-center four-electron bonds to the axial  $ClF$  bonds. This bonding scheme has previously been discussed in detail<sup>23</sup> for the related pseudo-trigonal bipyramidal  $ClF_2^-$  anion and, hence, will not be repeated.

TABLE V

Internal Force Constants of  $\text{ClF}_3\text{O}_2$ <sup>a,b</sup>

$f_D = 9.23$	$f_{\beta\beta} = 0.09$
$f_R = 3.35$	$f_{r\beta} = -f_{\beta r'} = 0.10$
$f_r = 2.70$	$f_{r\delta} = -f_{\delta r'} = 0.25$
$f_\alpha = 1.41$	$f_{D\alpha} = 0.61$
$f_\theta = 1.40$	$f_{\beta\delta} = -f_{\delta\beta'} = -0.16$
$f_\gamma = 1.33$	$f_{\delta\delta} = -f_{\delta\delta'} = -0.34$
$f_\delta = 1.30$	$f_{\delta\delta''} = -0.17$
$f_{DD} = -0.09$	$f_{\gamma\gamma} = -0.30$
$f_{rr} = -0.04$	$f_{R\alpha} = -0.37$

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(a) Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian<sup>2</sup>, and stretch-bend interaction constants in mdyn/radian.

(b) Only the values of the stretching force constants can be uniquely determined from the symmetry force constants; for the computation of the remaining constants, the following assumptions were made:  
 $f_{r\beta} = -f_{\beta r'}$ ,  $f_{r\delta} = -f_{\delta r'}$ ,  $f_{\beta\delta} = -f_{\delta\beta'}$ ,  $f_{\delta\delta} = -f_{\delta\delta'}$ , and  
 $f_{R\gamma} = f_{D\gamma} = f_{\alpha\gamma} = 0$ ;  $f_{\delta\delta'}$ ,  $f_{\delta\delta''}$ , and  $f_{\delta\delta'''}$  are the interactions between angles having a common oxygen, fluorine, and no common atom, respectively.

TABLE VI

ClF Stretching Force Constants (mdyn/Å) of  $\text{ClF}_3\text{O}_2^-$  Compared to Those of  
Pseudo-Trigonal Bipyramidal  $\text{ClF}_3\text{O}^8$ ,  $\text{ClF}_3^{22}$ ,  $\text{ClF}_2^-$ <sup>23</sup>, and  $\text{ClF}_2\text{O}_2^-$ <sup>9</sup>

	$f_R$	$f_r$	$f_{rr}$	$\frac{f_R - f_r}{f_R}$
$\text{ClF}_3$	4.2	2.7	0.36	0.36
$\text{ClF}_3\text{O}$	3.2	2.3	0.26	0.26
$\text{ClF}_3\text{O}_2^-$	3.4	2.7	-0.04	0.19
$\text{ClF}_2^-$	--	2.4	0.17	--
$\text{ClF}_2\text{O}_2^-$	--	1.6	-0.1	--

Inspection of Table VI also reveals that the value of  $f_r$  does not depend exclusively on the oxidation state of the central atom. Obviously, formal negative charges (as in the anions) and increasing oxygen substitution facilitate<sup>9</sup> the formation of semi-ionic bonds and, hence, counteract the influence of the oxidation state of the central atom. It is interesting to note that the relative contribution from semi-ionic bonding to the axial ClF bonds ( $= \frac{f_R - f}{f_R}$ ) decreases from  $\text{ClF}_3$  to  $\text{ClF}_3\text{O}$  and  $\text{ClF}_3\text{O}_2$  (see Table VI). This can be attributed to the decreasing electron density around the central atom with increasing oxidation state, thus making it more difficult to release electron density to the axial fluorine ligands as required for the formation of semi-ionic bonds.

In summary, the bonding in  $\text{ClF}_3\text{O}_2$  might be described by the following approximation:<sup>24</sup> The bonding of the three equatorial ligands, ignoring the second bond of the  $\text{Cl}=\text{O}$  double bond, is mainly due to a  $\text{sp}^2$  hybrid, whereas the bonding of the two axial ClF bonds involves one delocalized p-electron pair of the chlorine atom for the formation of a semi-ionic three-center four-electron  $\sigma$  bond.

The potential energy distribution<sup>25</sup> for  $\text{ClF}_3\text{O}_2$  was obtained from the internal force constants of Table V using a least square force field computation code without using least square refinement. With this code, we also verified that no computational errors had been made in the trial and error force field computation. The computed PED is given in Table VII. The results were normalized, but the sums do not in all cases add up to 1.0 since the less important terms are not listed. As can be seen from Table VII, most vibrations are reasonably characteristic, except for  $\nu_7$  and  $\nu_8$ , which are mixtures of the symmetry coordinates  $S_7$  and  $S_8$ .

TABLE VII

Potential Energy Distribution for ClF<sub>3</sub>O<sub>2</sub>

<u>Assignment</u>		<u>Frequency,</u>	<u>Potential Energy Distribution</u>
		<u>cm<sup>-1</sup></u>	
A <sub>1</sub>	v <sub>1</sub>	1093	0.99 f <sub>D</sub> + 0.06 f <sub>R</sub> - 0.06 f <sub>D<sub>α</sub></sub>
	v <sub>2</sub>	683	0.71 f <sub>R</sub> + 0.20 f <sub><sub>α</sub></sub> - 0.13 f <sub>R<sub>α</sub></sub> + 0.10 f <sub><sub>γ</sub></sub> + 0.05 f <sub>R</sub>
	v <sub>3</sub>	520	0.50 f <sub><sub>α</sub></sub> + 0.23 f <sub><sub>γ</sub></sub> + 0.22 f <sub>R</sub> + 0.12 f <sub>R<sub>α</sub></sub> - 0.05 f <sub><sub>γγ</sub></sub> - 0.05 f <sub>D<sub>α</sub></sub>
	v <sub>4</sub>	487	1.02 f <sub>r</sub>
	v <sub>5</sub>	286	0.61 f <sub><sub>β</sub></sub> + 0.28 f <sub><sub>δ</sub></sub> + 0.14 (f <sub><sub>ββ</sub></sub> - f <sub><sub>ββ'</sub></sub> ) + 0.07 (f <sub><sub>δδ'</sub></sub> - f <sub><sub>δδ</sub></sub> ) + 0.06 f <sub><sub>α</sub></sub>
A <sub>2</sub>	v <sub>6</sub>	417	1.15 f <sub><sub>δ</sub></sub> + 0.30 (f <sub><sub>δδ</sub></sub> - f <sub><sub>δδ'</sub></sub> ) - 0.15 f <sub><sub>δδ''</sub></sub>
B <sub>1</sub>	v <sub>7</sub>	695	0.86 f <sub>r</sub> + 0.39 f <sub><sub>δ</sub></sub> - 0.22 (f <sub><sub>rδ</sub></sub> + f <sub><sub>rδ'</sub></sub> ) + 0.10 (f <sub><sub>δδ</sub></sub> + f <sub><sub>δδ'</sub></sub> ) + 0.05 f <sub><sub>δδ''</sub></sub>
	v <sub>8</sub>	592	0.26 f <sub><sub>δ</sub></sub> + 0.25 f <sub>r</sub> + 0.10 (f <sub><sub>rδ</sub></sub> + f <sub><sub>rδ'</sub></sub> ) + 0.07 (f <sub><sub>δδ</sub></sub> + f <sub><sub>δδ'</sub></sub> ) + 0.06 f <sub><sub>β</sub></sub>
	v <sub>9</sub>	372	1.10 f <sub><sub>β</sub></sub> - 0.10 (f <sub><sub>ββ</sub></sub> + f <sub><sub>ββ'</sub></sub> ) + 0.08 f <sub><sub>δ</sub></sub> - 0.07 f <sub><sub>ββ''</sub></sub>
B <sub>2</sub>	v <sub>10</sub>	1327	0.93 f <sub>D</sub>
	v <sub>11</sub>	531	0.76 f <sub><sub>γ</sub></sub> + 0.16 f <sub><sub>γγ</sub></sub>
	v <sub>12</sub>	222	1.58 f <sub><sub>δ</sub></sub> - 0.41 (f <sub><sub>δδ</sub></sub> + f <sub><sub>δδ'</sub></sub> ) + 0.21 f <sub><sub>δδ''</sub></sub>

Association in the Liquid and Pure Solid. The relatively low boiling point ( $-21.58^{\circ}$ )<sup>2</sup> and Trouton constant ( $22.13$ )<sup>2</sup> of  $\text{ClF}_3\text{O}_2$  imply little association in the liquid phase. This prediction is confirmed by the vibrational spectra of the liquid and the neat solid which exhibit only minor frequency shifts when compared to the spectra of the gas and the matrix isolated solid. This finding is somewhat surprising since both  $\text{ClF}_3$ <sup>24</sup> and  $\text{ClF}_3\text{O}_2$ <sup>8</sup> show a pronounced tendency to associate in the liquid and solid state through bridges involving the axial fluorine atoms. For the pure solid, the infrared spectrum indicates the lowering of symmetry  $C_{2v}$  due to slight distortion or a lower site symmetry in the crystal because the  $A_2$  torsion mode, ideally forbidden in the infrared spectrum and not observed for the gas, becomes infrared active. Similarly, the symmetric axial  $\text{FClF}$  stretching mode,  $\nu_4(A_1)$ , which was not observed in the infrared spectrum of gaseous  $\text{ClF}_3\text{O}_2$ , gained for solid  $\text{ClF}_3\text{O}_2$  in relative intensity and was observed as a medium weak band.

Thermodynamic Properties. The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation<sup>26</sup>. These properties are given for the range  $0 - 2000^{\circ}\text{K}$  in Table VIII.

Acknowledgment. The authors wish to express their gratitude to Mr. R. D. Wilson for his help in the experimental efforts, to Drs. D. Pilipovich and C. J. Schack for helpful discussions, and to Dr. D. Lawson of the Jet Propulsion Laboratory for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch.

TABLE VIII

Thermodynamic Properties for  $\text{ClF}_3\text{O}_2$ 

<u>T, <math>^{\circ}\text{K}</math></u>	<u><math>C_p^0</math>, cal/<math>^{\circ}\text{K}</math>mol</u>	<u><math>H^0 - H_0^0</math>, kcal/mol</u>	<u><math>-(F^0 - H_0^0)/T</math>, cal/(mol deg)</u>	<u><math>S^0</math>, cal/ (mol deg)</u>
0	0	0	0	0
100	10.127	0.847	48.967	57.437
200	16.511	2.179	55.516	66.411
298.15	21.256	4.049	60.375	73.956
300	21.327	4.089	60.459	74.088
400	24.384	6.386	64.711	80.675
500	28.362	8.930	68.484	86.344
600	27.685	11.636	71.881	91.275
700	28.599	14.453	74.968	95.615
800	29.251	17.347	77.795	99.479
900	29.727	20.298	80.400	102.953
1000	30.085	23.289	82.816	106.105
1100	30.360	26.312	85.066	108.985
1200	30.574	29.354	87.171	111.637
1300	30.745	32.425	89.148	114.091
1400	30.883	35.507	91.012	116.375
1500	30.995	38.601	92.775	118.509
1600	31.089	41.705	94.447	120.513
1700	31.167	44.818	96.036	122.400
1800	31.233	47.938	97.551	124.183
1900	31.289	51.064	98.997	125.873
2000	31.337	54.196	100.382	127.480

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## DIAGRAM CAPTIONS

### Figure 1. Infrared and Raman Spectra of $\text{ClF}_3\text{O}_2$ .

Traces A and B represent the infrared spectrum of 22.3 and 230  $\mu$  mole, respectively, of neat solid  $\text{ClF}_3\text{O}_2$  at 4 $^{\circ}\text{K}$ ; traces C and D, the infrared spectrum of 0.89 and 20.6  $\mu$  mole, respectively, of  $\text{ClF}_3\text{O}_2$  in a  $\text{N}_2$  matrix (mole ratio 1:760) at 4 $^{\circ}\text{K}$ ; traces E to H, the infrared spectrum of gaseous  $\text{ClF}_3\text{O}_2$  at the denoted pressures in a 5 cm path-length cell; traces I and K, the Raman spectrum of gaseous  $\text{ClF}_3\text{O}_2$  at 4 atm pressure in a stainless steel cell with sapphire windows; traces L and M, the Raman spectrum at two different recorder voltages, respectively, of liquid  $\text{ClF}_3\text{O}_2$  in a Teflon FEP capillary at 25 $^{\circ}$ ; S indicates spectral slit-widths and P indicates polarized bands.

### Figure 2. Principal infrared bands of gaseous and $\text{N}_2$ matrix isolated $\text{ClF}_3\text{O}_2$ recorded at ten-fold scale expansion under higher resolution conditions.

The frequency denotations refer to the matrix isolation spectra. The frequency scale of the gas bands has been slightly shifted to line up the matrix band centers with the corresponding Q branches of the gas band contours.

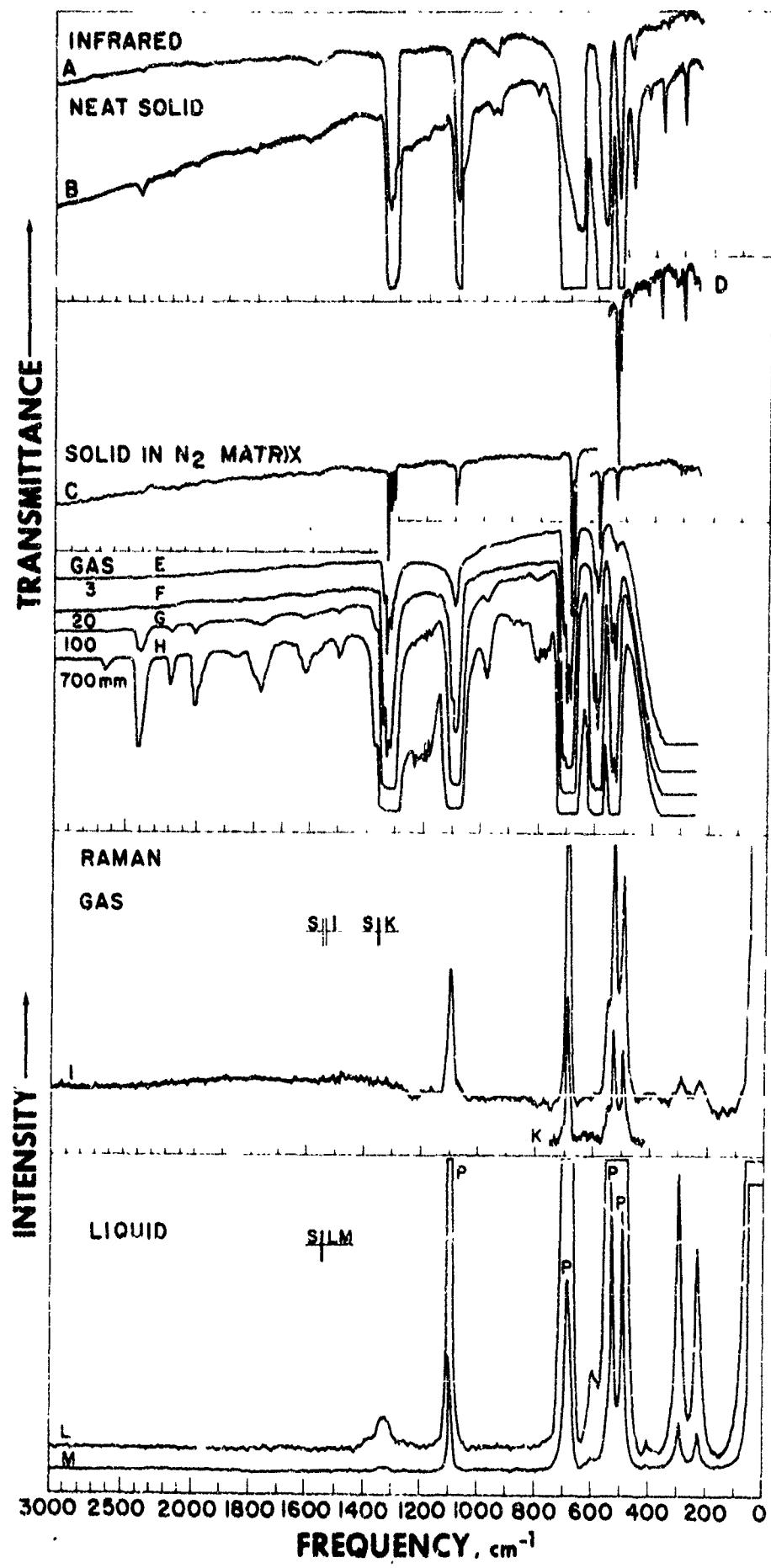


Figure 1.

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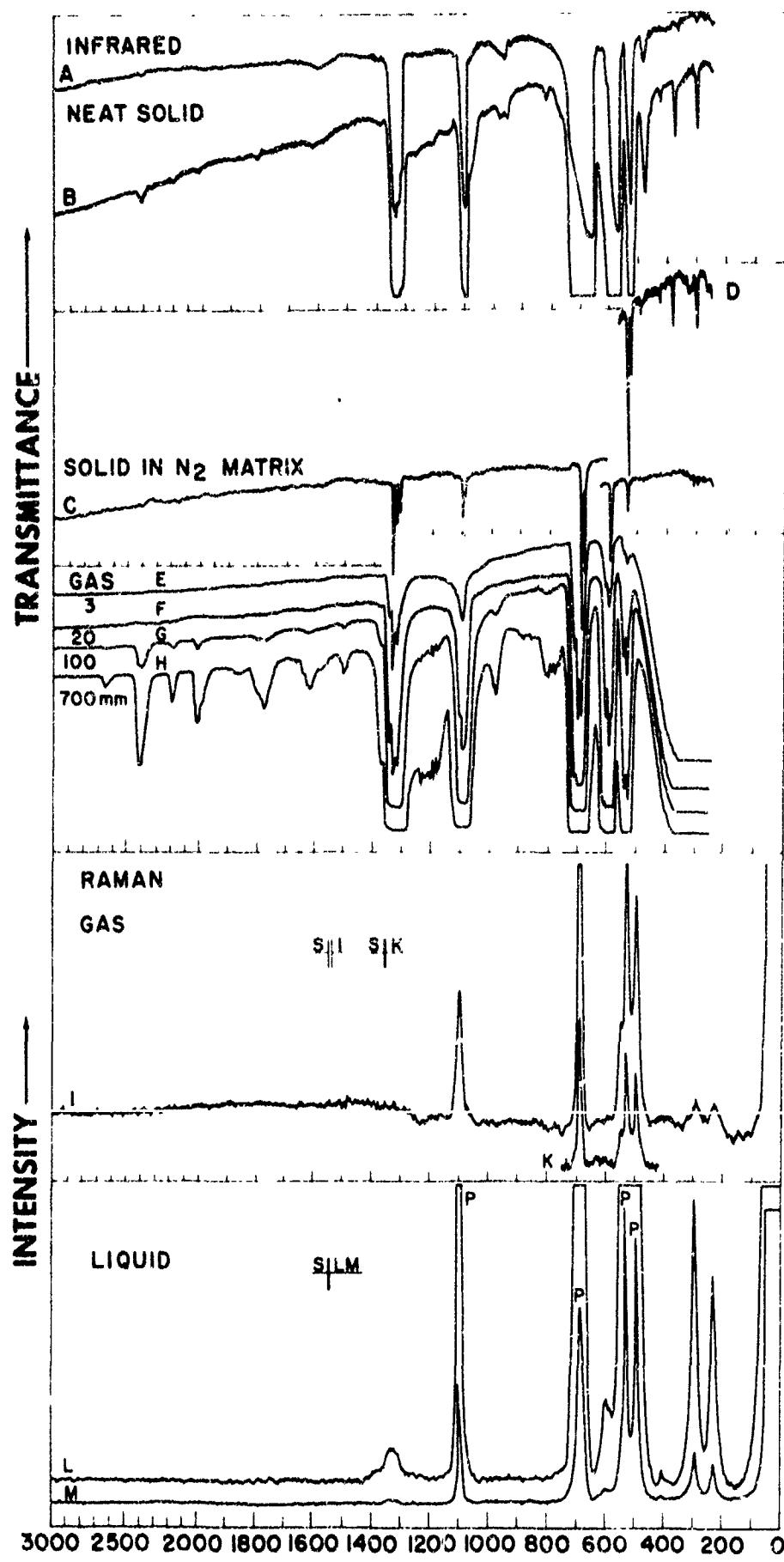
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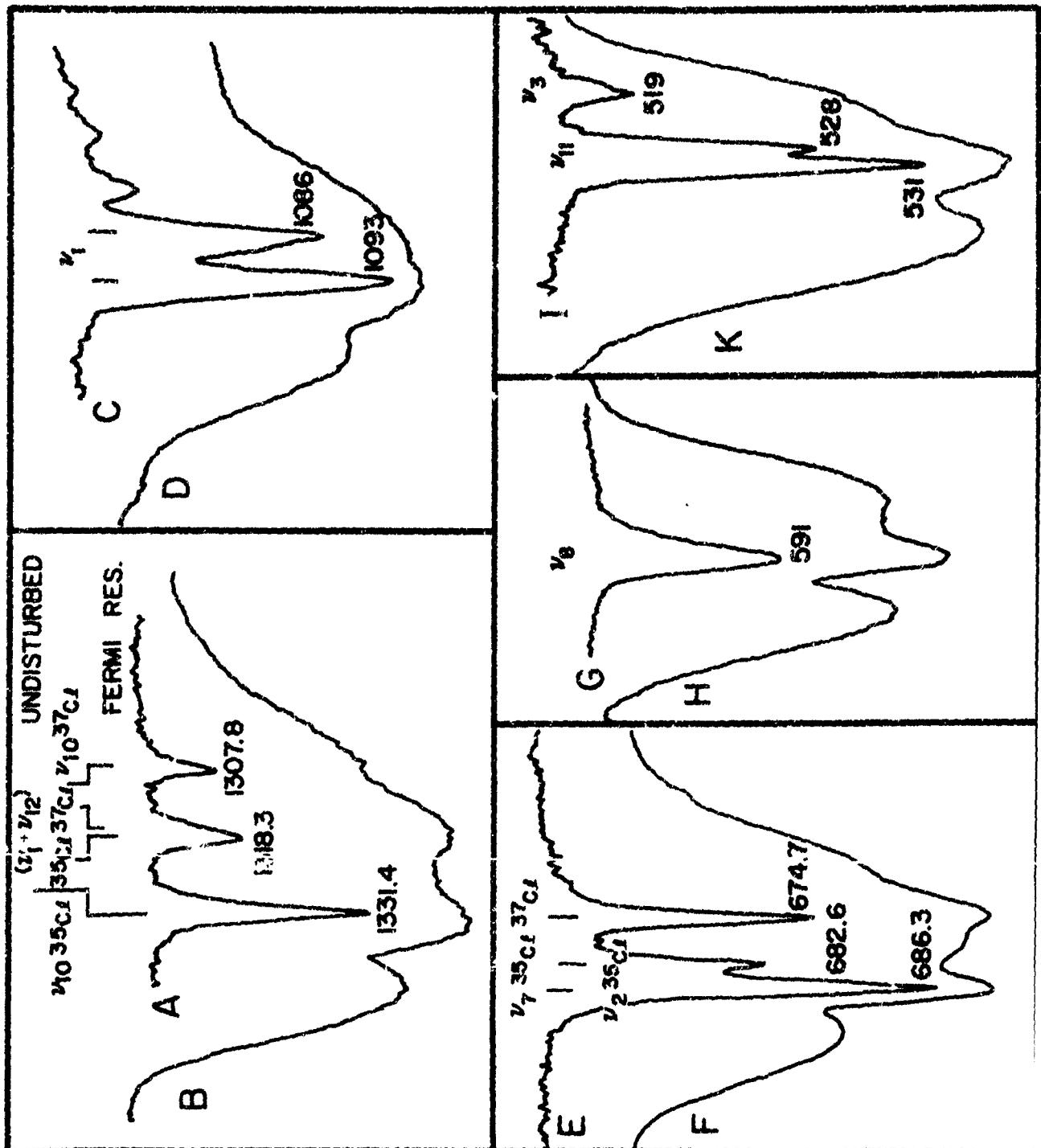


Figure 2.

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B-27/B-28

Contribution from Rocketdyne, a Division of North American Rockwell

Canoga Park, California 91304

The Difluoroperchloryl Cation,  $\text{ClO}_2\text{F}_2^+$

By Karl O. Christe\*, Richard D. Wilson, and E. C. Curtis

Received . . . . . 1972

Abstract

The reaction of  $\text{PClO}_2$  with  $\text{PtF}_6^-$  yields a product containing  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$ . A synthetic method is described that converts this salt into  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  or  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$ . All three salts are stable at 25° C and according to their infrared, Raman, and  $^{19}\text{F}$  nmr spectra are ionic in both the solid state and HF solution. The vibrational spectrum of  $\text{ClO}_2\text{F}_2^+$  closely resembles that of isoelectronic  $\text{SO}_2\text{F}_2$ , suggesting a pseudo-tetrahedral structure of symmetry  $\text{C}_{2v}$ . A modified valence force field is reported for  $\text{ClO}_2\text{F}_2^+$ .

Introduction

A preliminary note on the existence of  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  has recently been published<sup>1</sup> by Christe. This salt was prepared from  $\text{PClO}_2$  and  $\text{PtF}_6^-$ .<sup>1</sup> A detailed report on this interesting system, yielding under different reaction conditions  $\text{ClF}_6^+\text{PtF}_6^-$  has been given elsewhere.<sup>2</sup> A  $^{19}\text{F}$  nmr chemical shift of -310 ppm relative to

external  $\text{CFCI}_3$  has been tentatively assigned to  $\text{ClO}_2\text{F}_2^+$ .<sup>3</sup> A more complete characterization of the  $\text{ClO}_2\text{F}_2^+$  cation in the original  $\text{PtF}_6^-$  salt, however, was pre-empted by interference from the  $\text{PtF}_6^-$  anion and from substantial amounts of by-products such as  $\text{ClO}_2^+\text{PtF}_6^-$ . Consequently, efforts were made to prepare  $\text{ClO}_2\text{F}_2^+$  salts containing different anions and to eliminate the undesirable by-products. We have now succeeded in preparing  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  and  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$  and in more fully characterizing the  $\text{ClO}_2\text{F}_2^+$  cation. These results are described below.

### Experimental

Apparatus and Materials. The stainless steel - Teflon-PEP vacuum system, the glove box, the infrared, Raman, and  $^{19}\text{F}$  nmr spectrometers and sampling techniques, and the syntheses and purification of  $\text{PtF}_6$ ,  $\text{AsF}_5$ , and  $\text{FCIO}_2$  have been described elsewhere.<sup>2,3</sup> Nitryl fluoride, prepared from  $\text{N}_2\text{O}_4$  and  $\text{F}_2$ , and  $\text{BF}_3$  (from The Matheson Co.) were purified by fractional condensation. Debye-Scherrer x-ray diffraction powder patterns were taken as previously described.<sup>4</sup>

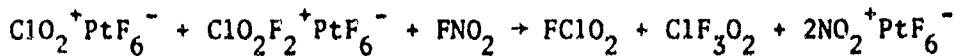
Syntheses of  $\text{ClO}_2\text{F}_2^+$  Salts. The synthesis of  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  has been described elsewhere.<sup>2</sup> For the synthesis of  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$ , a mixture of  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  (4.8 mmole) and  $\text{ClO}_2^+\text{PtF}_6^-$  (12.2 mmole) was treated in a passivated (with  $\text{ClF}_3$  and  $\text{BrF}_5$ ) 75 ml stainless steel cylinder with  $\text{FNO}_2$  (25.3 mmole) at  $-78^\circ$  for 48 hours. The reaction products volatile at  $25^\circ$  consisted of  $\text{FCIO}_2$ ,  $\text{ClF}_3\text{O}_2$ , and unreacted  $\text{FNO}_2$  and were separated by fractional condensation through a series of traps kept at  $-112^\circ$ ,  $-126^\circ$ ,  $-142^\circ$ , and  $-196^\circ$ . The  $-126^\circ$  fraction contained most of the  $\text{ClF}_3\text{O}_2$  and some  $\text{FCIO}_2$ . Attempts to further separate the  $\text{ClF}_3\text{O}_2$  and  $\text{FCIO}_2$  mixture by fractional condensation were unsuccessful. Consequently,

2.76 mmole of this mixture was combined with  $\text{BF}_3$  (3.00 mmole) at  $-196^\circ$  in a passivated Teflon-FEP ampoule and the temperature was cycled several times between  $-196^\circ$  and  $25^\circ$ . The product was kept at  $-78^\circ$  for several hours and unreacted  $\text{BF}_3$  (0.22 mmole) was removed at this temperature in vacuo. Removal of volatile material in vacuo was continued at  $20^\circ$ . The volatile material (2.60 mmole) consisted according to its infrared spectrum of a 1:1 mixture of  $\text{ClO}_2$  and  $\text{BF}_3$ . The white, solid, nonvolatile residue (280 mg = 1.46 mmole) was identified by infrared, Raman, and  $^{19}\text{F}$  nmr spectroscopy as  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$ .

For the preparation of the  $\text{AsF}_6^-$  salt,  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  (0.62 mmole) and  $\text{AsF}_5$  (1.43 mmole) were combined at  $-196^\circ$  in a passivated Teflon-FEP ampoule. The contents of the ampoule were kept at  $-78^\circ$  for 30 minutes and at  $25^\circ$  for 1 hour. Volatile products were removed at  $25^\circ$  and consisted of unreacted  $\text{AsF}_5$  (0.79 mmole) and  $\text{BF}_3$  (0.59 mmole). The white, stable solid weighed 185 mg (weight calcd for 0.62 mmole of  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$  = 183 mg) and was identified as  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$  by infrared, Raman, and  $^{19}\text{F}$  nmr spectroscopy.

#### Results and Discussion

Syntheses and Properties of  $\text{ClO}_2\text{F}_2^+$  Salts. The synthesis of  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  from  $\text{FCIO}_2$  and  $\text{PtF}_6^-$  and its temperature dependence has been discussed elsewhere.<sup>1,2</sup> Since the  $\text{PtF}_6^-$  anion interfered with the vibrational spectroscopic studies of  $\text{ClO}_2\text{F}_2^+$ , the  $\text{BF}_4^-$  and  $\text{AsF}_6^-$  salts were prepared according to the following scheme:



Unreacted  $\text{FNO}_2$  and some of the  $\text{FCIO}_2$  could be separated from  $\text{ClF}_3\text{O}_2$  by fractional condensation. The remaining  $\text{FCIO}_2$  was separated from  $\text{ClF}_3\text{O}_2$  by complexing with

$\text{BF}_3$ . Since the resulting  $\text{ClO}_2^+\text{BF}_4^-$  has a dissociation pressure<sup>5</sup> of 182 mm at 22.1° while  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  is stable, the former salt could be readily removed by pumping at 20°. Conversion of  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  to the corresponding  $\text{AsF}_6^-$  salt was accomplished through displacement of  $\text{BF}_4^-$  by the stronger Lewis acid  $\text{AsF}_5$ .

All three salts,  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$ ,  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$ , and  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$ , are solids, stable at 25°, and react violently with water or organic materials. The  $\text{PtF}_6^-$  compound is canary yellow, while those of  $\text{AsF}_6^-$  and  $\text{BF}_4^-$  are white. The salts dissolve in anhydrous HF without decomposing. They are crystallinic in the solid state and the x-ray powder diffraction patterns of  $\text{ClF}_2\text{O}_2^+\text{BF}_4^-$  and  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$  are listed in Table I. The powder pattern of  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  is much simpler than that of  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$ . This is not surprising since the anion and cation in the former salt are both approximately tetrahedral and of similar size. The powder pattern of  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  can be indexed on the basis of an orthorhombic unit cell with  $a = 5.45$ ,  $b = 7.23$ , and  $c = 13.00\text{\AA}$ . Assuming four molecules per unit cell and neglecting contributions from the highly charged central atoms to the volume,<sup>6,7</sup> a plausible average volume of  $16\text{\AA}^3$  per F or O atom is obtained. However, the agreement between the observed and calculated reflections is somewhat poor for several lines and, hence, the above unit cell dimensions are tentative.

The thermal stability of  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  is higher than those of  $\text{ClO}_2^+\text{BF}_4^-$ .<sup>5</sup>  $\text{ClF}_2^+\text{BF}_4^-$ ,<sup>8</sup> or other similar salts. This is in good agreement with the previously made correlations<sup>9</sup> between the stability of an adduct and the structure of the parent molecule and its ions. Thus, tetrahedral  $\text{ClO}_2\text{F}_2^+$  (see below) should be energetically much more favorable than trigonal bipyramidal  $\text{ClF}_3\text{O}_2$ .<sup>10</sup>

$^{19}\text{F}$  nmr Spectra. A broad singlet at -310 ppm relative to external  $\text{CFCl}_3$  has previously been observed for  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  at low concentration in anhydrous HF

Table I. X-Ray Powder Patterns for  
 $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  and  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$

$\text{ClO}_2\text{F}_2^+\text{BF}_4^-$		$\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$	
<u>d, Å</u>	<u>Intens</u>	<u>d, Å</u>	<u>Intens</u>
5.47	s	7.49	w
5.06	m	5.50	ms
4.37	ms	4.98	w
4.15	w	4.35	ms
3.70	vs	4.02	w
3.56	s	3.86	s
3.00	m	3.70	w
2.77	m	3.57	m
2.57	vw	3.40	mw
2.41	m	3.02	mw
2.18	s	2.77	m
2.08	s	2.69	m
1.86	ms	2.60	w
1.80	w	2.41	w
		2.30	w
		2.20	w
			1.34

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and was tentatively assigned to  $\text{ClO}_2\text{F}_2^+$ .<sup>3</sup> This tentative assignment is confirmed by the present study. The spectrum of  $\text{ClF}_2\text{O}_2^+\text{BF}_4^-$  in HF shows a strong temperature dependence. At 30° it consists of a single peak at 185 ppm relative to external  $\text{CPCl}_3$ . With decreasing temperature the peak at first becomes broader, then separates at about 0° into three signals at -301 ( $\text{ClO}_2\text{F}_2^+$ ), 146 ( $\text{BF}_4^-$ ),<sup>12</sup> and 194 ppm (HF) which become narrower with further decrease in temperature. The observed peak area ratio of approximately 2:1 for the 146 and -301 ppm signals confirms their assignment to  $\text{BF}_4^-$  and  $\text{ClO}_2\text{F}_2^+$ , respectively, and proves the ionic nature of the  $\text{ClF}_3\text{O}_2\text{BF}_3$  adduct in HF solution.

The spectrum of  $\text{ClF}_2\text{O}_2^+\text{AsF}_6^-$  in HF (which was acidified with  $\text{AsF}_5$ )<sup>3</sup> consists of two resonances at -307 ( $\text{ClO}_2\text{F}_2^+$ ) and 105 ppm (HF,  $\text{AsF}_5$ ,  $\text{AsF}_6^-$ )<sup>3</sup>, respectively. Rapid exchange between HF,  $\text{AsF}_5$ , and  $\text{AsF}_6^-$  preempted the measurement of the  $\text{ClO}_2\text{F}_2^+$  to  $\text{AsF}_6^-$  peak area ratio.

Vibrational Spectra. Fig. 1 shows the infrared and Raman spectrum of solid  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$  and the Raman spectrum of an HF solution of  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$ . Fig. 2 depicts the infrared and Raman spectrum of solid  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$ . Fig. 3 shows the infrared spectrum of a mixture of solid  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  and  $\text{ClO}_2^+\text{PtF}_6^-$ . The observed frequencies are listed in Table II and are compared with those reported for isoelectronic  $\text{SO}_2\text{F}_2$ .<sup>17</sup>

Inspection of Figures 1 to 3 and of Table II reveals that the spectra of  $\text{ClF}_3\text{O}_2\text{BF}_3$ ,  $\text{ClF}_3\text{O}_2\text{AsF}_5$ , and  $\text{ClF}_3\text{O}_2\text{PtF}_5$  contain the bands characteristic for  $\text{BF}_4^-$ ,<sup>13-16</sup>  $\text{AsF}_6^-$ ,<sup>16-19</sup> and  $\text{PtF}_6^-$ ,<sup>2,20</sup> respectively. Furthermore, the Raman spectra of  $\text{ClF}_3\text{O}_2\text{BF}_3$  are practically identical for both the solid and its HF solution. These observations together with the  $^{19}\text{F}$  nmr spectrum of the  $\text{BF}_3$  adduct in HF solution, establish that these adducts are ionic and contain the  $\text{ClO}_2\text{F}_2^+$  cation.

Table II. Vibrational Spectra of  $\text{ClO}_2\text{F}_2^+$  Salt Compared to that of  $\text{SnF}_2$

Wavenumber $\text{cm}^{-1}$	Assignment (Polar Group)	Observed Frequencies ( $\text{cm}^{-1}$ ) and Relative Intensities <sup>a</sup>						
		$\text{SnF}_2$ Liqu.	$\text{SnF}_2$ Gas	$\text{SnF}_2$ HF Sol.	$\text{ClO}_2\text{F}_2\text{BF}_4^-$ Liq.	$\text{ClO}_2\text{F}_2\text{BF}_4^-$ Solid	$\text{ClO}_2\text{F}_2\text{AF}_6^-$ Liq.	
1562	1497(1), <sup>b</sup> p	1567vs	1495(0.3), <sup>b</sup> p	1485(0.6) 1469(0.2)	1485(0.6) 1469(0.2)	1452(0.25) 1469	1489 1473	1340 2320
1270vs	1263(7), <sup>b</sup> p	1265vs	1252(4.4) 1244(1.5)	1245(3.9) 1237(1.3)	1245(3.9) 1237	1252 1244	1250 1242	2115w 1235
935	887(1)	885vs	834(0.7), <sup>b</sup> p	823(1.6) 771sh, <sup>b</sup> p	823(1.6) 772w	834(0.6)	823	827s 828
917vs	846(10), <sup>b</sup> p	846vs	761(10), <sup>b</sup> p	753(10)	754s	755s	754(0.1) 640vs,br	756s 642(2.5)
543	547(6), <sup>b</sup> p	540.5w	538(3.8) 533sh 538.4	534(4.7) 530sh 517(1.6)	534sh 529s 516w	534sh 529s 516w	514(0.4) 514s	532s 514s 514w
543vs	539(4), <sup>b</sup> p	536.5w	538(4.0), <sup>b</sup> p	537(7.9)	536w	535vs	535s 284w 265s	538 514 514w
								$\nu_1(\text{A}_1)$ $\nu_2(\text{A}_1)$ $\nu_3(\text{A}_1)$ $\nu_4(\text{E}_2)$ $\nu_5(\text{E}_2)$ $\nu_6(\text{F}_{2u})$ $\nu_7(\text{F}_{2g})$ $\nu_8(\text{F}_{2u})$
								$\nu_1(\text{A}_1)$ $\nu_2(\text{A}_1)$ $\nu_3(\text{A}_1)$ $\nu_4(\text{E}_2)$ $\nu_5(\text{E}_2)$ $\nu_6(\text{F}_{2u})$ $\nu_7(\text{F}_{2g})$ $\nu_8(\text{F}_{2u})$

<sup>a</sup> Uncorrected Raman Intensities; <sup>b</sup> P. Bender and J. M. Wood, Jr., J. Chem. Phys., 23, 1316 (1955); (c) D. R. Lide, Jr., D. E. Nelson, and J. J. Comford, Spectrochim. Acta, 21, 497 (1965), and G. R. Hazzard and H. K. Wilson, Ibid., 16, 579 (1960); (d) Assignments for  $\text{PtF}_6^-$  are made for simplicity on the basis of  $\text{PtF}_6^-$  though the site symmetry of  $\text{PtF}_6^-$  is lower than  $\text{SnF}_2$  (K. O. Christie, Inorg. Chem., in press).

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The assignments for the anions are well established and are summarized in Table II. Consequently, only the assignments for  $\text{ClO}_2\text{F}_2^+$  will be discussed in more detail. The  $\text{ClO}_2\text{F}_2^+$  cation is isoelectronic with  $\text{SO}_2\text{F}_2$  which was shown by microwave spectroscopy to possess symmetry  $C_{2v}$ .<sup>21</sup> The  $\text{SO}_2\text{F}_2$  structure can be derived from a tetrahedron with two oxygen and two fluorine ligands occupying the corners and with the O-S=O angle increased to  $123^\circ 58'$  and the F-S-F angle compressed to  $96^\circ 7'$ . Comparison of the bands due to  $\text{ClO}_2\text{F}_2^+$  with those previously reported<sup>12, 22, 23</sup> for  $\text{SO}_2\text{F}_2$  (see Table II) reveals a pronounced similarity indicating closely related structures and bonding. Therefore, assignments for  $\text{ClO}_2\text{F}_2^+$  were made by analogy with those of  $\text{SO}_2\text{F}_2$  which were reliably established by infrared,<sup>23</sup> Raman,<sup>22</sup> matrix isolation,<sup>12</sup> and microwave<sup>12</sup> studies. The analogy appears to include the triple and double coincidences between  $\nu_7(B_1)$ ,  $\nu_3(A_1)$ , and  $\nu_9(B_2)$  at about  $530 \text{ cm}^{-1}$  and between  $\nu_4(A_1)$  and  $\nu_5(A_2)$  at about  $390 \text{ cm}^{-1}$ , respectively. As for  $\text{SO}_2\text{F}_2$ ,<sup>12</sup> only tentative assignments to the individual modes can be made for the bands observed in the  $520 \text{ cm}^{-1}$  region.

The close analogy between the vibrational spectra of isoelectronic  $\text{ClO}_2\text{F}_2^+$  and  $\text{SO}_2\text{F}_2$  parallels those found for the isoelectronic pairs  $\text{ClF}_2\text{O}^+-\text{SF}_2\text{O}$ ,<sup>16</sup>  $\text{ClF}_6^+-\text{SF}_6$ ,<sup>2</sup>  $\text{ClF}_5^-\text{SF}_5$ ,<sup>24</sup> and  $\text{ClF}_4^+-\text{SF}_4$ .<sup>25</sup> It demonstrates the usefulness of knowing the vibrational spectra of the corresponding sulfur compounds for predicting and assigning those of the isoelectronic chlorine fluorides.

Additional evidence for the pseudo-tetrahedral structure of symmetry  $C_{2v}$  of  $\text{ClO}_2\text{F}_2^+$  consists of the  $^{35}\text{Cl} - ^{37}\text{Cl}$  isotopic splittings observed for the stretching modes (see Table III and Force Constant section).

Table III. Observed Frequencies ( $\text{cm}^{-1}$ ), Approximate Description of Modes, and Computed Symmetry and Non-Symmetry Internal Force Constants (Stretching Constants in dyne/ $\text{\AA}$ , Deformation Constants in dyne/ $\text{\AA}^2$ , and Stretch-Bend Interaction Constants in dyne/ $\text{\AA}$  radian) of  $\text{ClO}_2\text{F}_2^+$ . Values in Brackets are the Computed  $^{35}\text{Cl}-^{37}\text{Cl}$  Isotopic Shifts ( $\text{cm}^{-1}$ )

				Observed Isotopic Shifts
$\text{KOC10}$				
$\text{KPC1F}$				
$\nu_1$	1241	$\nu_{\text{sym}} \text{ClO}_2$	$F_{11} = f_D + f_{\text{DD}}$ $F_{12} = 2f_{\text{DR}}$	124 96 11.33[9.2]
$\nu_2$	756	$\nu_{\text{sym}} \text{ClF}_2$	$F_{22} = f_R + f_{\text{RR}}$ $F_{33} = 0.56f_E + 0.06f_B + 0.38f_{\text{BB}} + 0.72f_{\text{EF}} + 0.06f_{\text{EB}}$ $(f_{\text{BB}} + f_{\text{EF}} + f_{\text{EB}}) + 0.59f_{\text{BY}} - 0.93f_{\text{BY}}$	114 105 10.66[10.7]
$\nu_3$	514	$\nu_{\text{sym}} \text{ClO}_2$	$F_{34} = 0.52f_E + 0.13f_B - 0.45f_{\text{EF}} - 1.01f_{\text{EB}} + 0.13$ $(f_{\text{BB}} + f_{\text{EF}} + f_{\text{EB}}) + 0.31f_{\text{BY}} + 0.28f_{\text{BY}}$	109 103 10.12[12.4]
$\nu_4$	390	$\nu_{\text{sym}} \text{ClF}_2$	$F_{44} = 0.18f_E + 0.29f_B + 0.52f_{\text{EF}} - 0.91f_{\text{EB}} + 0.29$ $(f_{\text{BB}} + f_{\text{EF}} + f_{\text{EB}}) - 1.56f_{\text{BY}} + 0.63f_{\text{BY}}$	109 96 11.74[8.0]
$\nu_5$	390	$\tau$	$F_{55} = f_B - f_{\text{EB}} - f_{\text{BB}}' + f_{\text{BB}}''$	124 105 0.50
$\nu_6$	1479	$\nu_{\text{asy}} \text{ClO}_2$	$F_{66} = f_D - f_{\text{DD}}$ $F_{67} = \sqrt{2}(f_{\text{DB}} - f_{\text{DB}}')$	114 105 11.48[18.7]
$\nu_7$	553	$\delta_{\text{rock}} \text{ClO}_2$	$F_{77} = f_B + f_{\text{EF}} - f_{\text{BB}}' - f_{\text{BB}}''$	114 105 12.25[17.5]
$\nu_8$	830	$\nu_{\text{asy}} \text{ClF}_2$	$F_{88} = f_R - f_{\text{RR}}$ $F_{89} = \sqrt{2}(f_{\text{RB}} - f_{\text{RB}}')$	114 105 11.96[17.9]
$\nu_9$	514	$\delta_{\text{rock}} \text{ClF}_2$	$F_{99} = f_B - f_{\text{EF}} + f_{\text{BB}}' - f_{\text{BB}}''$	114 105 12.20
$f_D$				12.04
$f_{\text{DD}}$				- 0.66
$f_R$				- 1.07
$f_{\text{RR}}$				- 0.46
$f_{\text{EF}}$				- 4.63
$f_{\text{EB}}$				- 4.40
$f_{\text{BY}}$				- 4.53
$f_{\text{BB}}$				- 0.32
$f_{\text{BB}}'$				0.03

(a) Symmetry force constants not shown were assumed to be zero; (b)  $f_{\text{EF}}$ ,  $f_{\text{EB}}$ , and  $f_{\text{BB}}''$  refer to the interactions between the deformations of two angles having a common oxygen atom, a common fluorine atom, and no common oxygen or fluorine atom, respectively; (c) assumed values; (d) the numerical coefficients in the  $F$  matrix are based on the 124 and 96° bond angle geometry.

Force Constants. Three sets of force constants were computed for  $\text{ClO}_2\text{F}_2^+$  assuming different geometries. Two additional sets were computed requiring agreement between observed and computed  $^{35}\text{Cl} - ^{37}\text{Cl}$  isotopic shifts (see Table III). The potential and kinetic energy matrices were computed using a machine method.<sup>26</sup> The three different geometries adopted for  $\text{ClO}_2\text{F}_2^+$  differ only in the bond angles but not in the bond lengths. The bond lengths were estimated to be  $D(\text{ClO}) = 1.41$  and  $R(\text{ClF}) = 1.53\text{\AA}$  by comparison with related molecules and based on the correlation of Robinson<sup>27</sup> between frequencies and bond lengths. The bond angles of set I,  $\alpha(\text{OC1O}) = 124^\circ$ ,  $\beta(\text{CC1F}) = 108^\circ 15'$ , and  $\gamma(\text{FC1F}) = 96^\circ$ , were chosen to be identical with those of isoelectronic  $\text{SO}_2\text{F}_2$ .<sup>21</sup> For set III, tetrahedral bond angles were used and for set II a geometry was selected intermediate between those of sets I and III. The redundant coordinate was found numerically, and the deformation symmetry coordinates  $S_3$  and  $S_4$  were made orthogonal to it. To demonstrate that the redundancy condition was correct, it was verified that the frequencies of each block taken separately and the corresponding frequencies of the direct sum of all symmetry coordinates were the same.

The force constants were computed by trial and error with the aid of a computer, requiring exact fit between the observed and computed frequencies. The results are given in Table III where the force constants not shown were assumed to be zero. The values shown for sets I to III were the simplest set that would give an exact fit and, with the exception of  $F_{89}$ , represent a diagonal symmetry force field. By analogy with isoelectronic  $\text{SO}_2\text{F}_2$ ,<sup>28</sup> a nonzero value was required for  $F_{89}$  to fit the observed frequencies. Its value was assumed to be 0.5 to obtain a plausible value for  $F_{99}$ . Table III demonstrates the dependence of the force constants on the chosen bond angles and the impossibility to achieve a fit between

the observed and the computed  $^{35}\text{Cl} - ^{37}\text{Cl}$  isotopic shifts by simple variation of the bond angles. Numerical experiments confirmed that nonzero off-diagonal symmetry force constants are required to fit the observed isotopic shifts. The results for the more likely geometries I and II are listed as sets IV and V, respectively, in Table III. In the  $A_1$  symmetry block, the only interaction constant capable of sufficiently decreasing the  $\nu_1$  isotopic shift is  $F_{12}$ . The experimental data do not permit to distinguish between sets IV and V. However, the variation in the two force constants of greatest interest,  $f_D$  and  $f_R$ , is relatively small. Consequently, their values might be expected to approach those of a General Valence Force Field. A statistically meaningful uncertainty estimate cannot be made for the force constant values owing to their under-determined nature and to the lack of exact structural data. However, the numerical data of Table III allow some conclusions concerning the ranges of possible solutions. It should also be mentioned that the observed  $^{35}\text{Cl} - ^{37}\text{Cl}$  isotopic shifts varied slightly depending on the nature of the anion. In  $\text{ClO}_2\text{F}_2^+ \text{BF}_4^-$  for both the solid state and the HF solution, isotopic shifts of 7.5 and  $15.9 \text{ cm}^{-1}$  were observed for  $\nu_1(A_1)$  and  $\nu_6(B_1)$ , respectively. For solid  $\text{ClO}_2\text{F}_2^+ \text{PtF}_6^-$  the corresponding values were 8.5 and  $16.6 \text{ cm}^{-1}$ .

Of the internal force constants, the stretching force constants are of greatest interest since they can be used as a measure for the relative covalent bond strength. The stretching force constants of  $\text{ClO}_2\text{F}_2^+$  are listed in Table IV and compared to those of related molecules and ions. Comparison of the ClO stretching force constant of  $\text{ClO}_2\text{F}_2^+$  (12.1 mdyne / $\text{\AA}$ ) with those listed in Table IV shows that it is the highest value known for a ClO bond. This is not surprising, since the central atom in  $\text{ClO}_2\text{F}_2^+$  has a high oxidation state (+ VII), highly electronegative ligands, and a formal positive charge (cation). The influence of these

Table IV. Stretching Force Constants (mdyne / $\text{\AA}$ ) of  $\text{ClO}_2\text{F}_2^+$  Compared to Those of Related Compounds

	$f_{\text{ClO}}$		$f_{\text{ClF}}$	$f_{\text{ClF}}^{\text{a}}$
$\text{ClO}_2\text{F}_2^+$ <sup>b</sup>	12.1	$\text{ClF}_6^+$ <sup>i</sup>	4.7	
$\text{ClF}_2^0$ <sup>b</sup>	11.2	$\text{ClF}_2^+$ <sup>k</sup>	4.7	
$\text{FClO}_3^c$	9.4	$\text{ClF}_4^+$ <sup>l</sup>	4.5	, 3.2
$\text{ClF}_3^0$ <sup>d</sup>	9.4	$\text{ClO}_2\text{F}_2^+$	4.46	
$\text{FClO}_2^e$	9.1	$\text{ClF}_3^m$	4.2	, 2.7
		$\text{FClO}_3^c$	3.9	
$\text{ClO}_2^+$ <sup>f</sup>	9.0	$\text{ClF}_5^h$	3.5	, 2.7
$\text{ClF}_4^0$ <sup>g</sup>	8.9	$\text{ClF}_2^0$ <sup>b</sup>	3.4	
$\text{ClF}_2^0$ <sup>h</sup>	8.3	$\text{ClF}_3^0$ <sup>d</sup>	3.2	, 2.3
		$\text{FClO}_2^e$	2.5	
		$\text{ClF}_2^-$ <sup>o</sup>		2.4
		$\text{ClF}_4^-$ <sup>F</sup>		2.1
		$\text{ClF}_4^0$ <sup>g</sup>		1.9
		$\text{ClF}_2^0$ <sup>h</sup>		1.6

(a) ClF bonds for which strong contributions from semi-ionic 3 center-4 electron bonds can be invoked.

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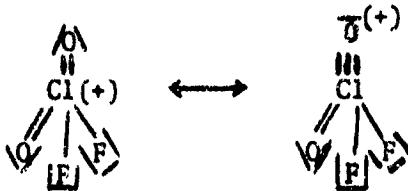
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factors on  $f_{ClO}$  has previously been discussed<sup>16</sup> for  $ClF_2O^+$  and, hence, will not be reiterated. By analogy with  $ClF_2O^+$ , the only other known species exhibiting a  $f_{ClO}$  value of similar magnitude, contributions from the following resonance structure



might be invoked<sup>16</sup> to explain the high  $f_{ClO}$  value. The value of the ClF stretching force constant (4.46 mdyne / $\text{\AA}$ ) falls within the range expected for a predominantly covalent ClF bond. The interpretation of relatively small differences (~0.3 mdyne / $\text{\AA}$ ) in the ClF stretching force constant values listed in Table IV should be done only with caution since most values were computed from underdetermined systems and might be significantly influenced by the chosen stretch-bend interaction constants.

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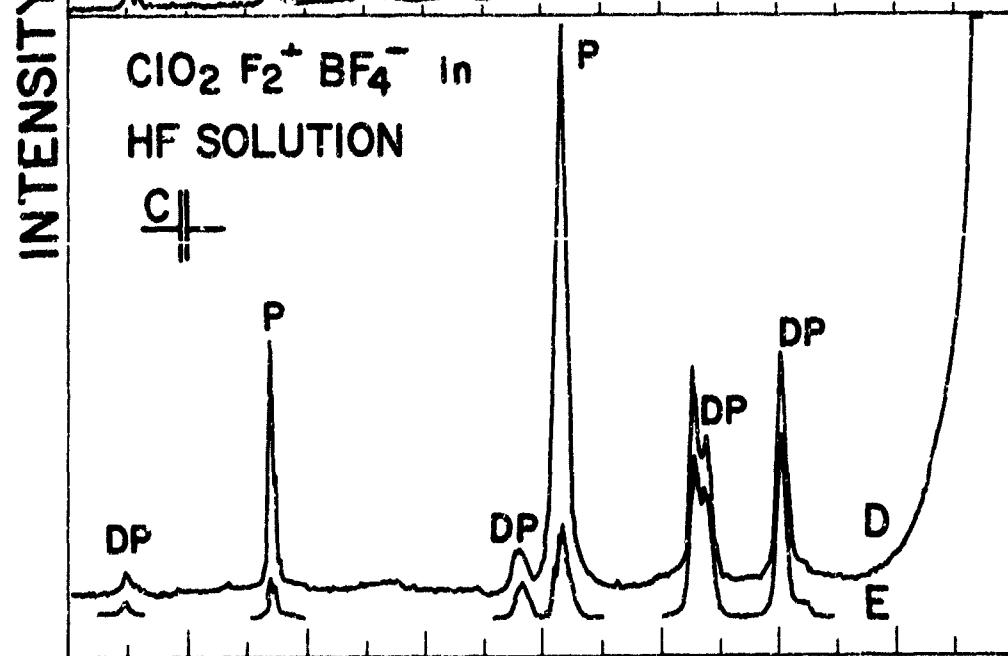
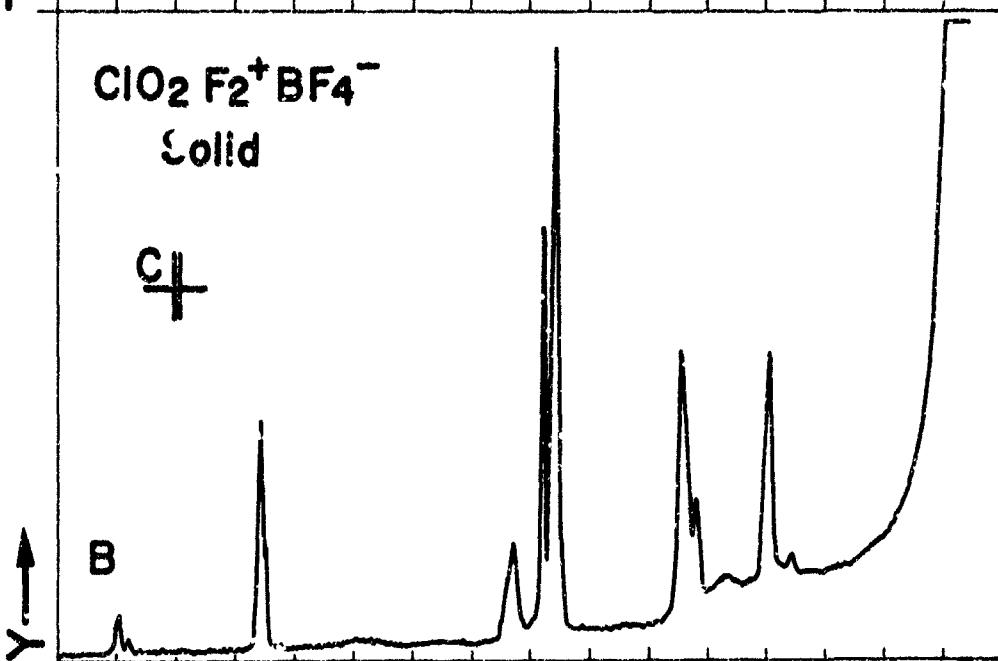
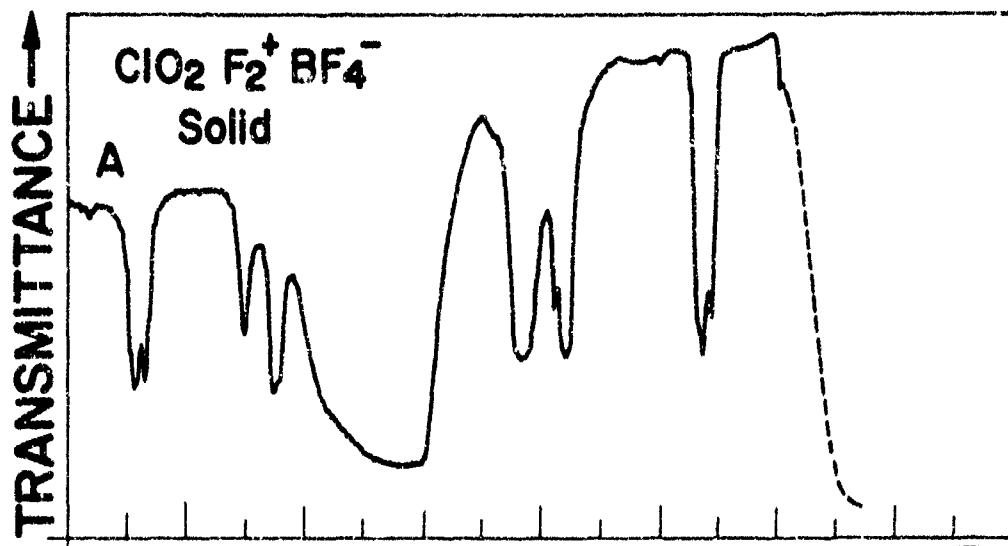
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Diagram Captions

Figure 1. Vibrational spectrum of  $\text{ClO}_2\text{F}_2^+\text{BF}_4^-$ . Trace A, infrared spectrum of the solid as a AgCl disk; trace B Raman spectrum of the solid; traces D and E Raman spectrum of the HF solution, incident polarization perpendicular and parallel, respectively; exciting line 4880 Å, C indicates spectral slit width.

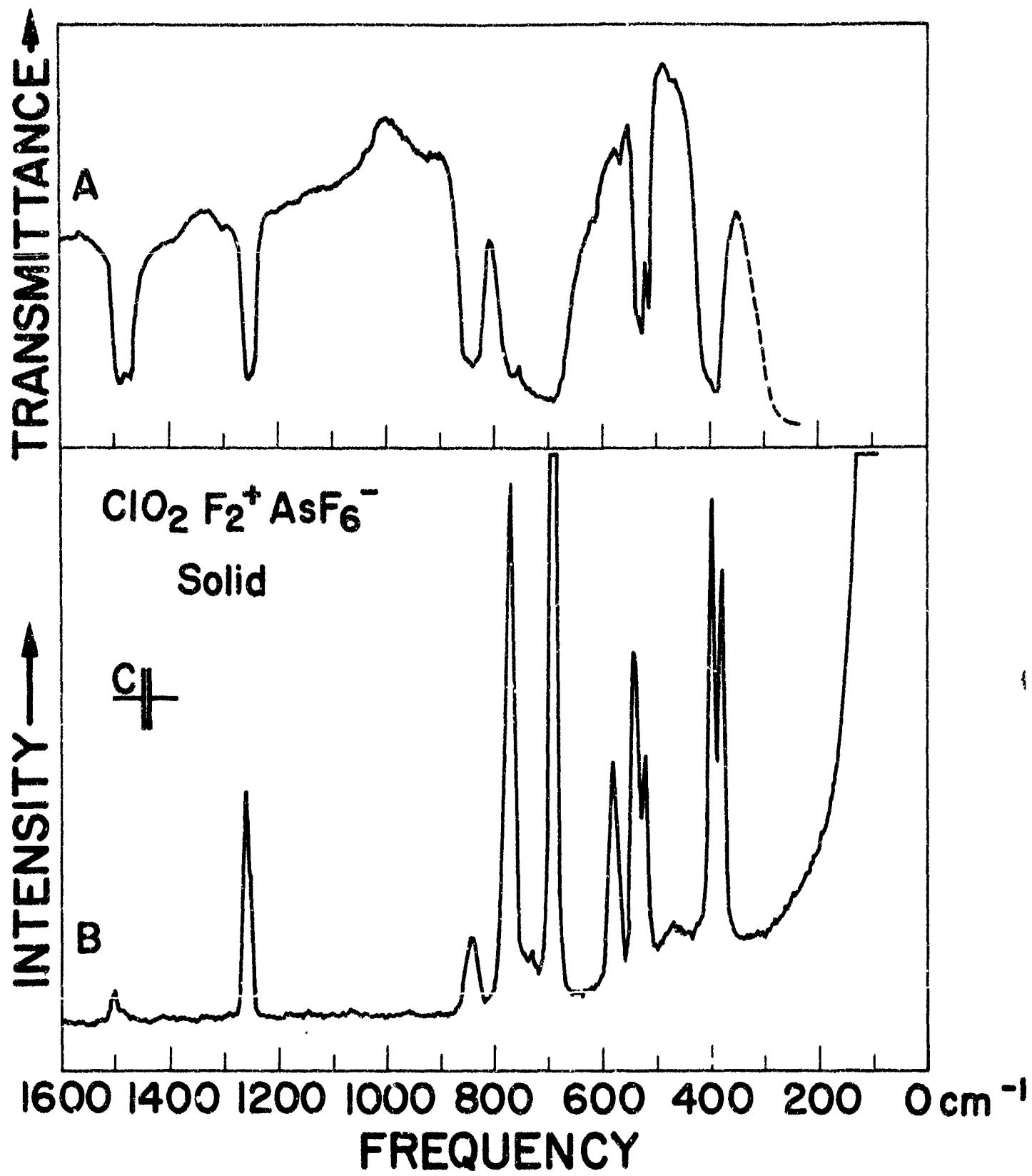
Figure 2. Vibrational spectrum of solid  $\text{ClO}_2\text{F}_2^+\text{AsF}_6^-$ . Trace A, infrared spectrum as AgCl disk; trace B, Raman spectrum; exciting line 4880 Å.

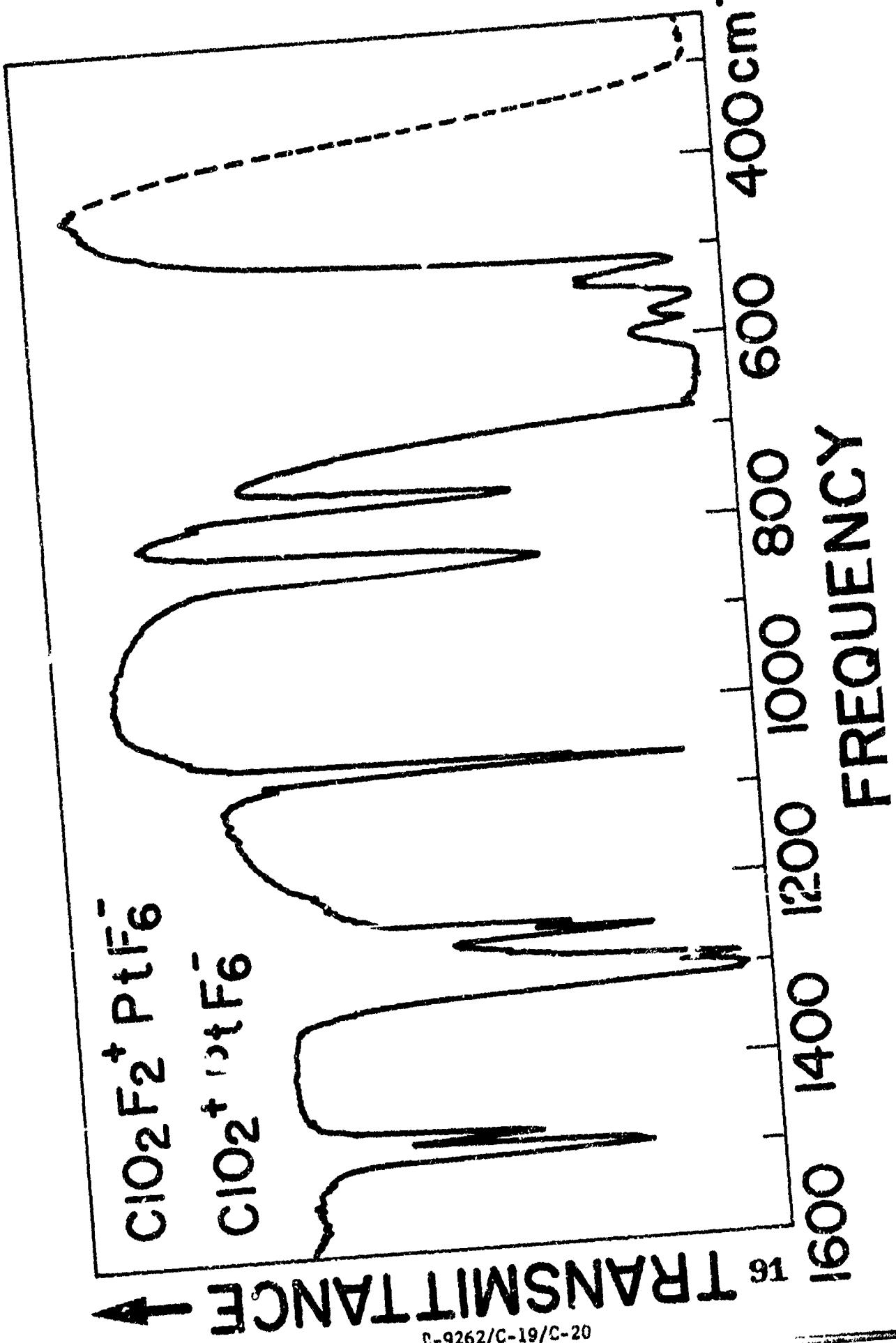
Figure 3. Infrared spectrum of a mixture of solid  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  and  $\text{ClO}_2^+\text{PtF}_6^-$  as a AgCl disk.



1600 1400 1200 1000 800 600 400 200, 0  $\text{cm}^{-1}$   
FREQUENCY

Figure 1.





Contribution from Rocketdyne, a Division of North American Rockwell,  
Canoga Park, California 91304

The Hexafluorochlorine (VII) Cation,  $\text{ClF}_6^+$ .

Synthesis and Vibrational Spectrum

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Abstract

The  $\text{ClF}_6^+$  cation was prepared in the form of its  $\text{PtF}_6^-$  salt from the reactions of  $\text{PtF}_6$  with either  $\text{FClO}_2$  or  $\text{ClF}_5$ . A displacement reaction between  $\text{ClF}_6^+\text{PtF}_6^-$  and  $\text{FN}_0$  at  $-78^\circ$  yielded only  $\text{ClF}_5$  and  $\text{F}_2$ , indicating that  $\text{ClF}_7$  cannot exist under the given reaction conditions. Attempts were unsuccessful to prepare either  $\text{ClF}_6^+\text{BF}_4^-$  by low temperature glow discharge of a  $\text{ClF}_5\text{-F}_2\text{-BF}_3$  mixture, or  $\text{ClF}_6^+$  salts from  $\text{ClF}_5$ ,  $\text{F}_2$ , and the Lewis acids  $\text{SbF}_5$ ,  $\text{AsF}_5$ , or  $\text{BF}_3$  at elevated temperatures and pressures, or  $\text{ClF}_4^0+$  salts either from  $\text{ClF}_3\text{O}$  and  $\text{PtF}_6$  or from  $\text{ClF}_3\text{O}$ ,  $\text{F}_2$ , and  $\text{SbF}_5$ . Iridium hexafluoride was found to be too weak an oxidizer to produce any heptavalent, chlorine containing cations from  $\text{FClO}_2$ . Vibrational spectra were recorded for  $\text{PtF}_6^-$  salts of  $\text{ClF}_6^+$ ,  $\text{ClF}_4^+$ ,  $\text{ClF}_2^+$ ,  $\text{ClF}_2\text{O}_2^+$ ,  $\text{ClF}_2\text{O}^+$ , and  $\text{ClO}_2^+$  and for  $\text{ClO}_2^+\text{IrF}_6^-$ . Modified valence force fields were computed for the  $\text{ClF}_6^+$ ,  $\text{PtF}_6^-$ , and  $\text{IrF}_6^-$  ions.

Introduction

Two preliminary notes on the synthesis of  $\text{ClF}_6^+\text{PtF}_6^-$  from  $\text{PtF}_6$  and chlorine fluorides or oxyfluorides have recently been published<sup>1,2</sup>, and the identity of

$\text{ClF}_6^+$  was established beyond doubt by  $^{19}\text{F}$  nmr spectroscopy<sup>2,3</sup>. The  $\text{ClF}_6^+$  cation is of particular interest for two reasons: (1) except for the recently discovered  $\text{ClO}_2\text{F}_2^+$  cation<sup>4</sup>, it is the only known heptavalent chlorine cation and (2) in addition to the  $\text{NF}_4^+$  salts<sup>5-9</sup>, it is the only known example of the synthesis of a fluoro cation derived from hitherto unknown compounds (i.e.,  $\text{NF}_5$  and  $\text{ClF}_7$ , respectively). In this paper, we give a full account of the synthesis, vibrational spectrum, and force constants of the  $\text{ClF}_6^+$  cation.

### Experimental

Apparatus and Materials. - The materials used in this work were manipulated in a well-passivated (with  $\text{ClF}_3$ ) 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellow-seal valves (Hoke, Inc., 425 IF4Y). Pressures were measured with a Heise, Bourdon Tube-type gauge ( $0-1500 \text{ mm} \pm 0.1\%$ ). Because of the rapid hydrolytic interaction with moisture, all materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin Elmer Models 337 and 457 spectrophotometers in the range  $4000 - 250 \text{ cm}^{-1}$ . The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The spectra of solids were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks mini pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded on either Cary Models 82 or 83 spectrophotometers using the 4880 and 6471  $\text{\AA}$  exciting lines, respectively. Glass melting point

capillaries or clear thin-walled Kel-F tubes were used as sample containers in the transverse viewing-transverse excitation technique.

Mass spectra were recorded on a Quad 300 (Electronic Associates Inc.) quadrupole mass spectrometer using a passivated all stainless steel inlet system.

Platinum hexafluoride was either purchased (from Ozark Mahoning Company) or freshly prepared by burning Pt wire in an  $F_2$  atmosphere at  $-196^{\circ}$ , according to the method of Weinstock and his coworkers<sup>10</sup>. Iridium hexafluoride was obtained from Ozark Mahoning Company. Prior to use, both  $IrF_6$  and  $PtF_6$  were purified by fractional condensation at  $-78^{\circ}$  in a dynamic vacuum. Arsenic pentafluoride (Ozark Mahoning Company) was purified by fractional condensation and  $SbF_5$  (Ozark Mahoning Company) by distillation. Chlorine pentafluoride (Rocketdyne) was stored over dry  $CaF$  to remove any  $ClF_3$  and purified by fractional condensation through traps kept at  $-112$  and  $-126^{\circ}$  with the material retained at  $-126^{\circ}$  being used. Fluorine (Rocketdyne) was passed over  $NaF$  to remove HF. Chloryl fluoride was prepared from  $KClO_3$  and  $ClF_3$ <sup>11</sup>,  $ClF_3O$  by fluorination of  $ClONO_2$ <sup>12</sup>, and  $FNO$  from  $NO$  and  $F_2$  at  $-196^{\circ}$ . The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra.

The  $FC1O_2$ - $PtF_6$  System. Platinum hexafluoride (17.0 mmole) and  $FC1O_2$  (46.1 mmole) were combined at  $-196^{\circ}$  in a passivated (with  $ClF_3$ ) 75-ml stainless steel cylinder. The mixture was allowed to warm up slowly to  $25^{\circ}$  and was kept at this temperature for three days. The cylinder was cooled to  $-196^{\circ}$  and 3.75 mmole of material volatile at this temperature was removed and identified as  $F_2$  by its vapor pressure and mass spectrum. The products volatile at  $25^{\circ}$  were separated by fractional condensation through traps kept at  $-78$ ,  $-126$ , and  $-196^{\circ}$ . The  $-126^{\circ}$  fraction consisted of  $FC1O_2$  (28.7 mmole) and the  $-196^{\circ}$  one of  $FC1O_2$  (0.3 mmole),  $ClF_5$  (0.1 mmole), and a small amount of  $FC1O_3$ . The cylinder contained a stable canary yellow solid (8.618 g),

which was identified by infrared spectroscopy as a mixture of  $\text{ClO}_2^+\text{PtF}_6^-$  and  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$ . Hence,  $\text{PtF}_6$  (17.0 mmole) had reacted with  $\text{FClO}_2$  (17.1 mmole) in a 1:1 mole ratio yielding  $\text{F}_2$  (3.75 mmole),  $\text{ClO}_2^+\text{PtF}_6^-$  (12.2 mmole = 4.594 g), and  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  (4.8 mmole = 2.000 g) as the main products.

Platinum hexafluoride (2.04 mmole) and  $\text{FClO}_2$  (3.98 mmole) were combined at  $-196^\circ$  in a passivated sapphire reaction tube (Varian, Model CS-4250-3). The reactor was rapidly warmed from  $-196^\circ$  to  $-78^\circ$  and kept at  $-78^\circ$  for 48 hours. At the end of this time period, the brown  $\text{PtF}_6$  color had completely disappeared and a canary yellow solid had formed. The reactor was cooled to  $-196^\circ$  and noncondensable material (0.33 mmole of  $\text{O}_2$ ) was removed. The product volatile at  $25^\circ$  consisted of  $\text{FClO}_2$  (1.03 mmole). The yellow, solid residue weighed 800 mg and was shown by infrared, Raman, and  $^{19}\text{F}$  nmr spectroscopy to be a mixture of  $\text{ClF}_6^+\text{PtF}_6^-$  and  $\text{ClO}_2^+\text{PtF}_6^-$  (weight calculated for a mixture of 1.70 mmole of  $\text{ClO}_2^+\text{PtF}_6^-$  and 0.34 mmole of  $\text{ClF}_6^+\text{PtF}_6^-$  = 796 mg). Hence,  $\text{PtF}_6$  (2.04 mmole) had reacted with  $\text{FClO}_2$  (2.05 mmole) in a 1:1 mole ratio producing  $\text{O}_2$  (0.33 mmole) and a 1:5 mole ratio mixture of  $\text{ClF}_6^+\text{PtF}_6^-$  and  $\text{ClO}_2^+\text{PtF}_6^-$ .

The  $\text{ClF}_6$ - $\text{PtF}_6$  System. Platinum hexafluoride (2.70 mmole) and  $\text{ClF}_5$  (3.90 mmole) were combined at  $-196^\circ$  in a passivated sapphire reactor. The mixture was kept at  $25^\circ$  for 24 hours. Since the brown  $\text{PtF}_6$  color was still very intense, the tube was exposed to unfiltered uv radiation from a Hanovia Model 616A high-pressure quartz mercury-vapor arc. After 24 hours of uv irradiation, the dark brown  $\text{PtF}_6$  color had disappeared and a yellow to brown solid had formed. The product was kept for 12 hours at  $-20^\circ$  without irradiation and its color changed to yellow-orange. The reactor was cooled to  $-196^\circ$  and noncondensables (2.58 mmole of  $\text{F}_2$ ) were removed. The reactor was warmed up to  $25^\circ$  and the volatile products were separated by fractional condensation. They consisted of  $\text{ClF}_5$  (1.08 mmole) and  $\text{ClF}_3$  (0.12 mmole). The yellow solid residue weighed 1.096 g

(weight calculated for a mixture of 0.84 mmole  $\text{ClF}_6^+\text{PtF}_6^-$  and 1.86 mmole  $\text{ClF}_2^+\text{PtF}_6^-$  = 1.097 g). The identity of this solid as  $\text{ClF}_2^+\text{PtF}_6^-$  and  $\text{ClF}_6^+\text{PtF}_6^-$  was verified by  $^{19}\text{F}$  nmr, infrared, and Raman spectroscopy. Hence,  $\text{PtF}_6$  (2.70 mmole) had reacted with  $\text{ClF}_5$  (2.70 mmole) producing  $\text{ClF}_6^+\text{PtF}_6^-$  (0.84 mmole),  $\text{ClF}_2^+\text{PtF}_6^-$  (1.86 mmole), and  $\text{F}_2$  (2.46 mmole). In addition, some of the  $\text{ClF}_5$  (0.12 mmole), which had been used in excess, had decomposed to  $\text{ClF}_3$  and  $\text{F}_2$ .

In a second experiment,  $\text{PtF}_6$  (5.26 mmole) and  $\text{ClF}_5$  (8.02 mmole) were combined at  $-196^\circ$  in a sapphire reactor. The mixture was exposed at ambient temperature to uv radiation from a Hanovia Model 616A high pressure Hg arc using a Pyrex-water filter. After 14 days of irradiation, the  $\text{PtF}_6$  color had disappeared and a yellow to orange solid had formed. The volatile products consisted of  $\text{F}_2$  (0.23 mmole),  $\text{ClF}_5$  (3.23 mmole), and a trace of  $\text{ClF}_3$ . The solid residue weighed 2.245 g and was, according to its infrared spectrum, a mixture of  $\text{ClF}_6^+\text{PtF}_6^-$  and  $\text{ClF}_4^+\text{PtF}_6^-$ . It appears that owing to the long reaction time and uv irradiation, some  $\text{PtF}_6$  (0.46 mmole as indicated by the  $\text{F}_2$  evolution and by the weight of the solid reaction product) had reacted with the container walls. Hence,  $\text{PtF}_6$  (4.80 mmole) had reacted with  $\text{ClF}_5$  (4.79 mmole) producing  $\text{ClF}_4^+\text{PtF}_6^-$  (2.40 mmole) and  $\text{ClF}_6^+\text{PtF}_6^-$  (2.40 mmole). The observed weight of the solid product (2.245 g) agreed well with that calculated (2.252 g) for the above reactions.

Displacement Reaction Between FNO and  $\text{ClF}_6^+\text{PtF}_6^-$ . To a mixture (0.390 g) of  $\text{ClF}_6^+\text{PtF}_6^-$  (0.30 mmole) and  $\text{ClF}_2^+\text{PtF}_6^-$  (0.66 mmole) in a passivated Teflon-FEP ampoule, FNO (6.75 mmole) was added at  $-196^\circ$ . The contents of the ampoule were kept at  $-78^\circ$  for 12 hours. The ampoule was cooled to  $-196^\circ$  and  $\text{F}_2$  (0.28 mmole) was removed. The products volatile at ambient temperature were separated by fractional condensation and consisted of FNO (5.76 mmole),  $\text{ClF}_3$  (0.64 mmole),

and  $\text{ClF}_5$  (0.27 mmole). The yellow, solid residue weighed 0.329 g (calculated weight for 0.96 mmole of  $\text{NO}^+\text{PtF}_6^-$  = 0.326 g) and was identified by its infrared spectrum as  $\text{NO}^+\text{PtF}_6^-$ .

Reaction Between  $\text{ClF}_3\text{O}$  and  $\text{PtF}_6$ . Platinum hexafluoride (1.87 mmole) and  $\text{ClF}_3\text{O}$  (4.71 mmole) were combined at  $-196^\circ$  in a sapphire reaction tube. When the mixture was allowed to warm to  $25^\circ$ , a rapid reaction with gas evolution occurred and the characteristic  $\text{PtF}_6$  color disappeared within a few minutes. The mixture was kept at  $25^\circ$  for several hours and was then cooled to  $-196^\circ$ . Fluorine (0.78 mmole) was removed at  $-196^\circ$  and  $\text{ClF}_3\text{O}$  (2.05 mmole),  $\text{ClF}_5$  (0.14 mmole), and  $\text{FClO}_2$  (0.48 mmole) at  $25^\circ$ . The canary yellow residue weighed 0.749 g (weight calculated for 1.87 mmole of  $\text{ClF}_2\text{O}^+\text{PtF}_6^-$  = 0.746 g) and was identified as  $\text{ClF}_2\text{O}^+\text{PtF}_6^-$  by its infrared, Raman, and  $^{19}\text{F}$  nmr spectrum.

In another experiment,  $\text{PtF}_6$  (2.12 mmole) and  $\text{ClF}_3\text{O}$  (5.51 mmole) were allowed to interact at  $-45^\circ$  for 12 hours. The volatile products consisted of  $\text{F}_2$  (1.60 mmole),  $\text{ClF}_3\text{O}$  (3.35 mmole),  $\text{FClO}_2$  (0.07 mmole), and a small amount of  $\text{ClF}_5$  and  $\text{PtF}_6$ . The yellow solid residue weighed 0.847 g (weight calculated for 2.12 mmole of  $\text{ClF}_2\text{O}^+\text{PtF}_6^-$  = 0.845 g). The infrared spectrum of the solid showed it to be mainly  $\text{ClF}_2\text{O}^+\text{PtF}_6^-$ , but also revealed the presence of smaller amounts of  $\text{ClO}_2\text{F}_2^+$  and  $\text{ClF}_6^+$  salts.

Reaction Between  $\text{FClO}_2$  and  $\text{IrF}_6$ . Chloryl fluoride (2.57 mmole) and  $\text{IrF}_6$  (1.96 mmole) were combined at  $-196^\circ$  in a sapphire reactor. The mixture was kept at  $-78^\circ$  for 48 hours, then cooled to  $-196^\circ$ . All products were condensed at this temperature. At  $25^\circ$ , almost all of the starting materials were recovered unchanged except for 0.011 g of a yellowish solid which was identified by its infrared spectrum as  $\text{ClO}_2^+\text{IrF}_6^-$ . The unreacted starting materials were condensed

back into the reactor and kept at 25° for 11 days. After this period, the product still showed the original brown color but had partially solidified. The mixture was cooled to -196° at which temperature 0.03 mmole of noncondensable material was removed. The material volatile at 25° consisted of  $\text{IrF}_6$  (1.12 mmole),  $\text{ClF}_2$  (1.88 mmole), and  $\text{ClF}_5$  (0.21 mmole). The yellow crystalline solid weighed 0.147 g (0.39 mmole) and was identified by infrared and Raman spectroscopy as  $\text{ClF}_2^{+}\text{IrF}_6^{-}$ .

Attempted Syntheses of  $\text{ClF}_6^{+}\text{SbF}_6^{-}$ ,  $\text{ClF}_6^{+}\text{AsF}_6^{-}$ ,  $\text{ClF}_6^{+}\text{BF}_4^{-}$ , and  $\text{ClF}_4\text{O}^{+}\text{SbF}_6^{-}$ .

When mixtures of  $\text{ClF}_5$ ,  $\text{F}_2$ , and  $\text{AsF}_5$  in different mole ratios were heated in Monel cylinders for five to ten days at 125 to 145° under autogenous pressures of 500 to 1000 psi, only unreacted starting materials were recovered in addition to very small amounts of metal  $\text{AsF}_6^{-}$  salts. Heating the mixture to 160° resulted in partial breakdown of  $\text{ClF}_5$  to  $\text{ClF}_3$  and  $\text{F}_2$ .

Heating a  $\text{BF}_3$ ,  $\text{F}_2$ , and  $\text{ClF}_5$  mixture (mole ratio 1:2.7:2) for eight days to 95° under an autogenous pressure of 450 psi did not result in the formation of a solid product.

Mixtures of  $\text{ClF}_5$ ,  $\text{F}_2$ , and  $\text{SbF}_5$  (mole ratio 1:5:3) were heated for three to 40 days in Monel cylinders at 140 to 225° under autogenous pressures of ~ 1000 psi. At 140° and three days reaction time, no  $\text{F}_2$  consumption was observed. At 160° and 25 days reaction time, 6.5% of the  $\text{F}_2$  used was consumed due to attack on the cylinder. The solid product was a mixture of  $\text{ClF}_2^{+}$ ,  $\text{ClF}_4^{+}$ ,  $\text{Ni}^{++}$ , and  $\text{Cu}^{++}$  salts of  $\text{SbF}_6^{-} \cdot x\text{SbF}_5$ . Controlled vacuum pyrolysis of this solid resulted in the evolution of  $\text{ClF}_5$  at lower and of  $\text{ClF}_3$  at higher temperatures. The composition of the solid residues of this stepwise pyrolysis was monitored by infrared and Raman spectroscopy. It was shown that the more stable component having strong

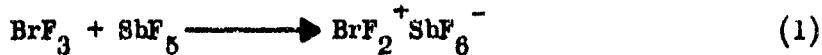
absorptions in the infrared and Raman spectrum at 825 and 836  $\text{cm}^{-1}$  generated only  $\text{ClF}_3$  when heated in the presence of  $\text{CaF}$ . When the reaction between  $\text{ClF}_5$ ,  $\text{F}_2$ , and  $\text{SbF}_5$  was carried out at  $225^\circ$ ,  $\text{ClF}_2^+\text{SbF}_6^-$  was formed with  $\text{F}_2$  evolution.

Glow discharge of a  $\text{BF}_3$ ,  $\text{F}_2$ , and  $\text{ClF}_5$  mixture (mole ratio 1:1.42:1) at  $-78^\circ$  in a Pyrex apparatus at pressures ranging from 20 to 50 mm produced only  $\text{ClF}_2^+\text{BF}_4^-$  and no  $\text{ClF}_6^+$  salt.

Heating a mixture of  $\text{ClF}_3$ ,  $\text{F}_2$ , and  $\text{SbF}_5$  (mole ratio 1:10:5) in a Monel cylinder to  $135^\circ$  for six days under an autogenous pressure of 600 psi produced exclusively  $\text{ClF}_2^+\text{SbF}_6^- \cdot x\text{SbF}_5$ .

#### Results and Discussion

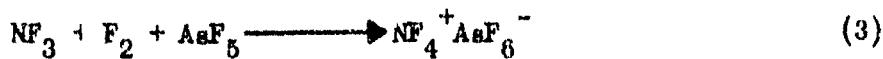
Synthesis of  $\text{ClF}_6^+$  Salts. Complex fluoro cations of the type  $\text{XF}_{y-1}^+$  are generally prepared through fluorine abstraction from the parent compound  $\text{XF}_y$  by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus<sup>13</sup> for  $\text{BrF}_3$ :



The synthesis of a fluoro cation from a lower fluoride, according to:



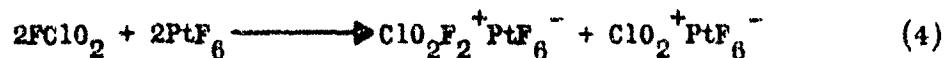
is pre-empted by the fact that fluorine is the most electronegative element. Hence,  $\text{F}^+$  should be extremely difficult if not impossible to prepare by chemical means. The first and only known synthesis of a fluoro cation derived from a nonexisting parent compound was achieved<sup>5,9</sup> in 1966, according to:



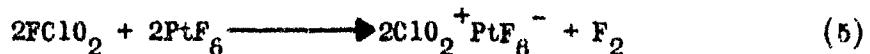
This synthesis involved either glow-discharge<sup>5</sup> or elevated temperature and pressure<sup>9</sup>. Since tetrahedral and octahedral species exhibit outstanding stability, as demonstrated by  $CF_4$  and  $SF_6$ , the successful synthesis of  $NF_4^+$  suggested the feasibility of synthesizing  $ClF_6^+$  salts.

The application of glow-discharge to the synthesis of  $ClF_6^+$  salts is limited to the  $ClF_5-F_2-BF_3$  system. Stronger Lewis acids, such as  $AsF_5$ , form adducts with  $ClF_5$ <sup>14</sup>, thus preventing the use of the low-temperature glow-discharge technique. In the case of  $BF_3$ , we did not successfully prepare  $ClF_6^+ BF_4^-$ , owing to rapid breakdown of  $ClF_5$  to  $ClF_3$  and  $F_2$ , followed by removal of the  $ClF_3$  from the gas phase by complex formation with  $BF_3$ <sup>15</sup>. The possible utility of the second technique, involving elevated temperature and pressure, for the synthesis of  $ClF_6^+$  salts was also examined with  $BF_3$ ,  $AsF_5$ , or  $SbF_5$  as Lewis Acids. At lower temperatures, no fluorination of  $ClF_5$  occurred, whereas at higher temperatures, breakdown of  $ClF_5$  to  $ClF_3$  and  $F_2$  was observed. Since  $ClF_2^+$  salts are thermally more stable than the corresponding  $ClF_4^+$  salts,  $ClF_3$  was continuously removed from the  $ClF_5 \rightleftharpoons ClF_3 + F_2$  equilibrium by complexing until essentially all the  $ClF_5$  was converted to  $ClF_2^+$  and  $F_2$ .

Since the techniques which had successfully been used for the synthesis of  $NF_4^+$  salts did not result in  $ClF_6^+$ , other fluorinating agents were investigated. Of particular interest were the third transition series hexafluorides which exhibit an astonishing oxidizing power<sup>16</sup>. It was found<sup>17</sup> that  $PtF_6$  and  $FeCl_2$ , when combined at  $-195^\circ$  and allowed to slowly warm up to  $25^\circ$ , interacted according to:

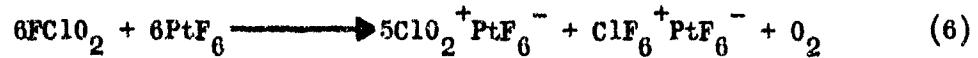


The yield of  $\text{ClO}_2\text{F}_2^+$  was not 50% as expected from the above equation, but generally about 25% owing to the following competing reaction:



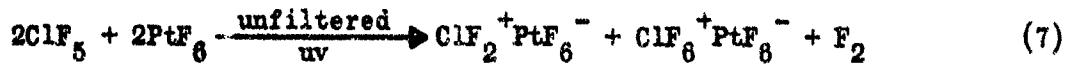
In some of the experiments, small amounts of  $\text{ClF}_6^+ \text{PtF}_6^-$  (see below) or  $\text{ClF}_5$  and  $\text{FClO}_3$  were observed, depending on the exact reaction conditions. The formation of some  $\text{FClO}_3$  is not surprising since it is known that  $\text{FClO}_2$  readily interacts with nascent oxygen to yield  $\text{FClO}_3$ .<sup>18,19</sup>

Attempts to suppress the competing reaction (5) by changing the reaction conditions (rapid warm up from  $-196$  to  $-78^\circ$  and completion of the reaction at  $-78^\circ$ ) resulted in an entirely different course for the reaction:

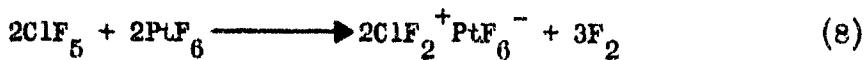


The observed material balance was in excellent agreement with equation (6) and the identity of  $\text{ClF}_6^+$  was unequivocally established by  $^{19}\text{F}$  nmr spectroscopy.<sup>20</sup> Further modification of the reaction conditions (rapid warm up of the  $\text{FClO}_2$ - $\text{PtF}_6$  mixture from  $-196$  to either  $-78$  or  $25^\circ$  and completion of the reaction at  $25^\circ$ ) did not produce detectable amounts of either  $\text{ClO}_2\text{F}_2^+$  or  $\text{ClF}_6^+ \text{PtF}_6^-$ , but only  $\text{ClO}_2^+ \text{PtF}_6^-$  and  $\text{ClF}_5$ ,  $\text{F}_2$ , and  $\text{O}_2$ . This indicates that the nature of the reaction products are more influenced by the warm up rate of the starting materials from  $-196$  to about  $-78^\circ$  than by the final reaction temperature. Slow warm up favors the formation of  $\text{ClO}_2\text{F}_2^+$ , whereas rapid warm up yields  $\text{ClF}_6^+ \text{PtF}_6^-$  or  $\text{ClF}_5$  and  $\text{F}_2$ .

The above results for the  $\text{FClO}_2\text{-PtF}_6$  system indicated that  $\text{ClF}_5$  might be an important intermediate in the formation of  $\text{ClF}_6^+$ . In order to prove the correctness of this assumption and in order to possibly increase the yield of  $\text{ClF}_6^+$ , which according to equation (6) can be at best  $1/6$  based on  $\text{PtF}_6$ , we have studied also the  $\text{ClF}_5\text{-PtF}_6$  system. For the latter system, Roberto reported<sup>1</sup> the formation of a  $\text{ClF}_6^+$  salt. Owing to the slow reaction rates in the  $\text{ClF}_5\text{-PtF}_6$  system, we have used uv radiation. Two reactions were carried out at  $25^\circ$ . When unfiltered uv radiation was used, the reaction was complete in several hours, according to:



and



The relative contribution from (7) and (8) were 62 and 38%, respectively. In addition, some of the  $\text{ClF}_5$ , which had been used in excess, was recovered in the form of  $\text{ClF}_3$  and  $\text{F}_2$ .

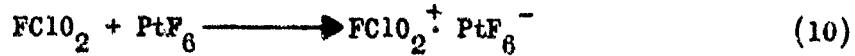
Using a Pyrex-water filter, a reaction time of two weeks was required with the products being:



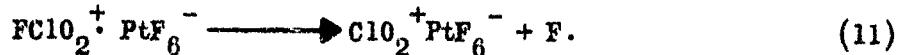
Since unfiltered uv light can decompose  $\text{ClF}_5$  into  $\text{ClF}_3 \sim \text{F}_2$ <sup>21</sup> and since  $\text{ClF}_2^+$  salts are more stable than  $\text{ClF}_4^+$  salts<sup>14</sup>, the displacement of  $\text{ClF}_4^+$  by  $\text{ClF}_3$ , observed for (7), is not surprising. The identity of the  $\text{ClF}_3^+$  salt obtained from the  $\text{FClO}_2\text{-PtF}_6$  system with that from the  $\text{ClF}_5\text{-PtF}_6$  system was established by infrared, Raman, and <sup>19</sup>F nmr spectroscopy.

The unusual nature of these reactions and products ask for a possible rationalization. In spite of the complexity of the  $\text{FClO}_2$ - $\text{PtF}_6$  system, the following assumptions appear plausible:

(a) An initial electron transfer from  $\text{FClO}_2$  to  $\text{PtF}_6$ , according to:

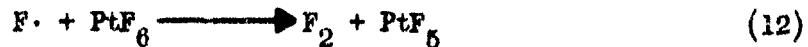


(b) The resulting  $\text{FClO}_2^+$  radical cation could either stabilize by generating an active fluorine radical, according to:

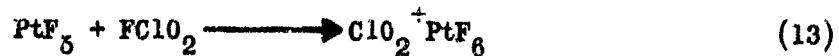


or act itself as the active fluorinating agent, depending upon the relative life times of these two radicals.

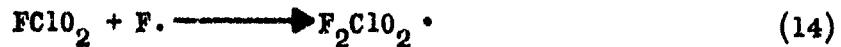
(c) In both cases ( $\text{F.}$  or  $\text{ClO}_2^+$ ), the radical might react either with  $\text{PtF}_6$  with  $\text{F}_2$  evolution:



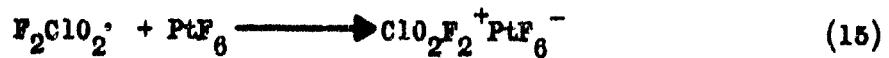
followed by:



or with  $\text{FClO}_2$ :



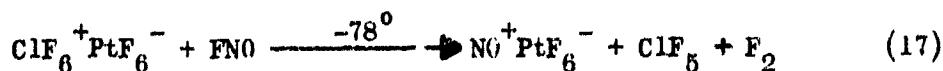
(d) The resulting  $\text{F}_2\text{ClO}_2^+$  radical could readily stabilize by transfer of an electron to  $\text{PtF}_6$ :



This sequence would account for the formation of  $\text{ClO}_2\text{F}_2^+$  and for the competitive  $\text{F}_2$  evolution reaction. Similarly, the formation of  $\text{ClF}_6^+$  from  $\text{ClF}_5$  and  $\text{PtF}_6^-$  might involve an intermediate  $\text{ClF}_5^+$  radical cation and suggests a search for radical cations in these systems. The formation of  $\text{ClF}_6^+$  from  $\text{FClO}_2$  might involve either an intermediate  $\text{ClF}_5$  molecule or the direct fluorination of  $\text{ClO}_2\text{F}_2^+$  to  $\text{ClF}_6^+$ . A definitive answer to these interesting questions concerning the most important intermediates is beyond the scope of the present study.

Properties of  $\text{ClF}_6^+$  Salts. The  $\text{ClF}_6^+\text{PtF}_6^-$  salts are canary yellow solids. They were stored at  $25^\circ$  in Teflon-FEP containers for several months without noticeable decomposition and formed stable HF solutions. They are very powerful oxidizers and react explosively with organic materials or water. Contrary to a previous statement<sup>1</sup>, no evidence was found during our investigation that the  $\text{ClF}_6^+$  salts themselves can be explosive.

On the Existence of  $\text{ClF}_7$ . A displacement reaction between  $\text{ClF}_6^+\text{PtF}_6^-$  and  $\text{FN}_0$  was carried out under conditions similar to those which had successfully been used for the synthesis of  $\text{ClF}_3\text{O}_2$  from  $\text{ClO}_2\text{F}_2^+\text{PtF}_6^-$  and  $\text{FN}_0^4$ . Since  $\text{ClF}_6^+\text{PtF}_6^-$  can be considered as a Lewis acid adduct between  $\text{ClF}_7$  and  $\text{PtF}_5$ , the products from the  $\text{FN}_0$  displacement reaction allow some conclusions concerning the stability of the hypothetical compound  $\text{ClF}_7$ . The following results were obtained for the displacement reaction:



This indicates that  $\text{ClF}_7$  under the given reaction conditions ( $-78^\circ$ ) cannot exist.

Iridium Hexafluoride Reactions. Replacement of  $\text{PtF}_6^-$  by  $\text{IrF}_6^-$  in the  $\text{FClO}_2$  reaction did not result in an oxidative fluorination of  $\text{Cl}(\text{+V})$  to  $\text{Cl}(\text{+VII})$ . At  $25^\circ$  and long reaction times, only  $\text{ClO}_2^+\text{IrF}_6^-$  and  $\text{ClF}_5$  were formed in moderate yields. This demonstrates that  $\text{IrF}_6^-$  is a weaker fluorinating oxidizer than  $\text{PtF}_6^-$  as has previously been demonstrated by Bartlett<sup>16</sup>.

Attempted Synthesis of  $\text{ClF}_4^+$  Salts. The successful syntheses<sup>1,2,4</sup> of the  $\text{ClO}_2\text{F}_2^+$  and the  $\text{ClF}_6^+$  cation suggest the possible synthesis of the intermediate  $\text{ClF}_4^+$  cation from  $\text{ClF}_3\text{O}$  and  $\text{PtF}_6^-$ . At  $25^\circ$ , the main reaction was:



In addition, small amounts of  $\text{FClO}_2$  and  $\text{ClF}_5$  were observed among the volatile reaction products. When the reaction temperature was lowered to  $-45^\circ$ , the main products were again  $\text{ClF}_2\text{O}^+\text{PtF}_6^-$  and  $\text{F}_2$ . However, small amounts of  $\text{ClO}_2\text{F}_2^+$  and  $\text{ClF}_6^+\text{PtF}_6^-$  had also formed. No evidence for the presence of any  $\text{ClF}_4^+$  could be obtained. This suggests that tetrahedral  $\text{ClF}_2\text{O}_2^+$  and octahedral  $\text{ClF}_6^+$  are more favorable products than the pseudo trigonal bipyramidal  $\text{ClF}_4^+$ . The formation of small amounts of  $\text{ClO}_2\text{F}_2^+$  and  $\text{ClF}_6^+$  (or  $\text{FClO}_2$  and  $\text{ClF}_5$ ) might be due either to the decomposition of an unstable intermediate, such as  $\text{ClF}_4^+$ , into  $\text{ClO}_2\text{F}_2^+$  and  $\text{ClF}_6^+$ , or at least partially to the formation of some  $\text{FClO}_2$  from the difficult to handle  $\text{ClF}_3\text{O}$ .<sup>12</sup> Attempts to synthesize  $\text{ClF}_4^+\text{SbF}_6^-$  from  $\text{ClF}_3\text{O}\text{-F}_2\text{-SbF}_5$  at elevated temperature and pressure produced exclusively  $\text{ClF}_2\text{O}^+\text{SbF}_6^- \cdot x\text{SbF}_5$ .

Vibrational Spectra. The infrared and Raman spectra of the solid reaction products are shown by Figures 1 and 2, respectively. The spectrum of  $\text{ClF}_2\text{O}^+\text{PtF}_6^-$  was identical to that previously reported<sup>22</sup> and hence, is not depicted. Attempts to record the Raman spectrum of the  $\text{ClF}_4^+\text{PtF}_6^- - \text{ClF}_6^+\text{PtF}_6^-$  mixture were

unsuccessful owing to rapid sample decomposition by the laser beam. From a large number of experiments, those spectra and products were selected which showed the least amounts of by-products. Depending upon the exact reaction conditions, however, the products sometimes were more complex mixtures of  $\text{ClO}_2^+$ ,  $\text{ClO}_2\text{F}_2^+$ , and  $\text{ClF}_6^+$ , or of  $\text{ClF}_2^+$ ,  $\text{ClF}_4^+$ , and  $\text{ClF}_6^+$ . The observed frequencies are listed in Table I.

Since most products contain the  $\text{PtF}_6^-$  anion, its spectrum will be discussed first. The simplest spectrum is that of  $\text{NO}^+\text{PtF}_6^-$ . Our observed spectrum is in good agreement with that previously reported<sup>16,23,24</sup> for this compound. In addition to the reported bands, we have observed an infrared band at  $268 \text{ cm}^{-1}$ . The crystal structure of  $\text{O}_2^+\text{PtF}_6^-$  (which is isomorphous with  $\text{NO}^+\text{PtF}_6^-$ )<sup>16</sup> has been determined<sup>15</sup>. It was shown that  $\text{PtF}_6^-$  is approximately octahedral<sup>25</sup>; however, its site symmetry<sup>26</sup> is lower than  $\text{O}_h$ . This site symmetry lowering can cause splitting of most of the bands and violations of the selection rules expected for symmetry  $\text{O}_h$ . Since the crystal structures and, hence, the actual site symmetries of  $\text{PtF}_6^-$  in the other chlorine fluoride salts are unknown and since the observed splittings are relatively small, the assignments for  $\text{PtF}_6^-$  in Table I were made based on the group symmetry  $\text{O}_h$ . In addition to the previously assigned bands<sup>16,23,24</sup>, the antisymmetric deformation,  $\nu_4$  ( $\text{F}_{1u}$ ), and the normally inactive  $\nu_6$  ( $\text{F}_{2u}$ ) mode were observed at about  $265$  and  $180 \text{ cm}^{-1}$ , respectively. The spectrum observed for  $\text{IrF}_6^-$  is in good agreement with that of  $\text{PtF}_6^-$ . In addition to the previously reported<sup>23</sup> bands, the  $\nu_4$  and  $\nu_6$  modes were also observed for  $\text{IrF}_6^-$ .

The vibrational spectra of  $\text{ClO}_2^+$ <sup>27</sup>,  $\text{ClF}_2\text{O}_2^+$ <sup>4,28</sup>,  $\text{ClF}_2^+$ <sup>29,30</sup>,  $\text{ClF}_2\text{O}^+$ <sup>22,31,32</sup>, and  $\text{ClF}_4^+$ <sup>33</sup> have been reported elsewhere. The assignments given in Table I are in excellent agreement with those previously given for these ions and, hence, require no further discussion. Assignments for  $\text{ClF}_6^+$ , whose identity and

TABLE 1. VIBRATIONAL SPE

HO <sup>+</sup> PtF <sub>6</sub> <sup>-</sup>			ClO <sub>2</sub> <sup>+</sup> , ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup> PtF <sub>6</sub> <sup>-</sup>			ClO <sub>2</sub>	
Obsd Frequency, cm <sup>-1</sup>	IR	Assignment for PtF <sub>6</sub> <sup>-</sup> in O <sub>3</sub>	Obsd Frequency, cm <sup>-1</sup>	IR	Assignment for ClO <sub>2</sub> <sup>+</sup> and ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup> in C <sub>2v</sub> , for PtF <sub>6</sub> <sup>-</sup> in O <sub>3</sub>	Obsd Frequency, cm <sup>-1</sup>	IR
2383 nm			2340			2340	
2329 nm	2328 (0+)	WHD	2320	w	v <sub>1</sub> + v <sub>3</sub> (B <sub>1</sub> )ClO <sub>2</sub> <sup>+</sup>	2320	w
1280 w, br		v <sub>1</sub> + v <sub>3</sub> (F <sub>1u</sub> )PtF <sub>6</sub> <sup>-</sup>	2118 vw		2v <sub>1</sub> (A <sub>1</sub> )ClO <sub>2</sub> <sup>+</sup>	1297 vs	1299 (0.3)
1212 w, br		v <sub>2</sub> + v <sub>3</sub> (F <sub>1u</sub> + F <sub>2u</sub> )PtF <sub>6</sub> <sup>-</sup>	1486	s	v <sub>6</sub> (A <sub>1</sub> )ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	1283 s	1285 (0.1)
880 vw, br		v <sub>3</sub> + v <sub>5</sub> (A <sub>2u</sub> + E <sub>u</sub> + F <sub>1u</sub> + F <sub>2u</sub> )PtF <sub>6</sub> <sup>-</sup>	1470	s	v <sub>3</sub> (B <sub>1</sub> )ClO <sub>2</sub> <sup>+</sup>	1210 w	
630 vw, br		v <sub>2</sub> + v <sub>4</sub> (F <sub>1u</sub> + F <sub>2u</sub> )PtF <sub>6</sub> <sup>-</sup>	1297 vs	1299 (0.5)	v <sub>3</sub> (B <sub>1</sub> )ClO <sub>2</sub> <sup>+</sup>	1053 s	1054 (2.0)
640 vs, br		v <sub>3</sub> (F <sub>1u</sub> )PtF <sub>6</sub> <sup>-</sup>	1283 s	1285 (0.17)	v <sub>1</sub> (A <sub>1</sub> )ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	1049 s	
	644 (10)	v <sub>1</sub> (A <sub>1g</sub> )PtF <sub>6</sub> <sup>-</sup>	1265	s	v <sub>1</sub> (A <sub>1</sub> )ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	890 s	
	589 (0+)	v <sub>2</sub> (E <sub>g</sub> )PtF <sub>6</sub> <sup>-</sup>	1210 v		v <sub>2</sub> + v <sub>3</sub> (F <sub>1u</sub> + F <sub>2u</sub> )PtF <sub>6</sub> <sup>-</sup>	640	vs
578 s	579 (2)	v <sub>2</sub> (E <sub>g</sub> )PtF <sub>6</sub> <sup>-</sup>	1052 s	1051 (2.7)	v <sub>1</sub> (A <sub>1</sub> )ClO <sub>2</sub> <sup>+</sup>	620	vs
295 nm		v <sub>4</sub> (F <sub>1u</sub> )PtF <sub>6</sub> <sup>-</sup>	1047 s		v <sub>8</sub> (B <sub>2</sub> )ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	610	(3.1)
269 nm			827 s		v <sub>2</sub> (A <sub>1</sub> )ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	644	(10)
	249 (4)	v <sub>5</sub> (F <sub>2g</sub> )PtF <sub>6</sub> <sup>-</sup>	756 s	754 (0.1)	v <sub>3</sub> (B <sub>2</sub> )ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	580 nm	580 (1.0)
	236 sh		640 vs	617 (2.5)	v <sub>3</sub> (F <sub>1u</sub> )PtF <sub>6</sub> <sup>-</sup>	552 s	554 (2.5)
			642 (10)		v <sub>1</sub> (A <sub>1g</sub> )PtF <sub>6</sub> <sup>-</sup>	514 s	518 (0.6)
			560 v	564 (1.3)	v <sub>6</sub> (B <sub>2</sub> )PtF <sub>6</sub> <sup>-</sup>	240	(4.5)
			552 s	552 (1.0)	v <sub>2</sub> (E <sub>g</sub> )PtF <sub>6</sub> <sup>-</sup>	185	(0.2)
			530 sh		v <sub>3</sub> (A <sub>1</sub> ), v <sub>7</sub> (B <sub>1</sub> ), v <sub>9</sub> (B <sub>2</sub> )ClF <sub>2</sub> O <sub>2</sub> <sup>+</sup>	130	(0.1)
			514 s	514 (0.4)	v <sub>2</sub> (A <sub>1</sub> )ClO <sub>2</sub> <sup>+</sup>	90	(1.0)
			284 w		v <sub>6</sub> (F <sub>1u</sub> )PtF <sub>6</sub> <sup>-</sup>		
			230 (2.9)		v <sub>5</sub> (F <sub>2g</sub> )PtF <sub>6</sub> <sup>-</sup>		
			180 (0+)		v <sub>6</sub> (F <sub>2u</sub> )PtF <sub>6</sub> <sup>-</sup>		

1. VIBRATIONAL SPECTRA OF SEVERAL  $\text{PtF}_6^-$  SALTS AND OF  $\text{ClO}_2^+\text{IrF}_6^-$  AND THEIR ASSIGNMENT - RAMAN INTEGRALS

$\text{ClO}_2^+\text{PtF}_6^-$	$\text{ClO}_2^+\text{ClF}_6^-\text{PtF}_6^-$		$\text{ClF}_2^+\text{ClF}_6^-\text{PtF}_6^-$		$\text{ClF}_2\text{O}^+\text{PtF}_6^-$	
	Obsd Frequency, $\text{cm}^{-1}$	Assignment for $\text{ClO}_2^+$ in $\text{C}_{2v}$ , for $\text{ClF}_6^-$ and $\text{PtF}_6^-$ in $\text{O}_h$	Obsd Frequency, $\text{cm}^{-1}$	Assignment for $\text{ClF}_2^+$ and $\text{PtF}_6^-$ in $\text{C}_{2v}$	Obsd Frequency, $\text{cm}^{-1}$	Assignment for $\text{ClF}_2\text{O}^+$ in $\text{C}_s$ , for $\text{PtF}_6^-$
2340	v		1776 v	$v_3 + v_5(\text{B}_1)\text{ClF}_2^+$	1326 ns	$v_1(\text{A}^+)\text{ClF}_2\text{O}^+$
2320		$v_1 + v_3(\text{B}_1)\text{ClO}_2^+$	1954 v	$v_1 + v_3(\text{F}_{1u})\text{ClF}_2^+$	1313 nc	$v_1(\text{A}^+)\text{ClF}_2\text{O}^+$
1297 vs	1299 (0.3)	$v_3(\text{B}_1)\text{ClO}_2^+$	1910 v	$v_2 + v_3(\text{F}_{1u} + \text{F}_{2u})\text{ClF}_2^+$	737 s	$v_2(\text{A}^+)\text{ClF}_2\text{O}^+$
1283 s	1285 (0.1)		1298	$v_3(\text{B}_1)\text{ClO}_2^+$	705 s	$v_3(\text{A}^+)\text{ClF}_2\text{O}^+$
1210 w		$v_2 + v_3(\text{F}_{1u} + \text{F}_{2u})\text{PtF}_6^-$	1284	$v_1 + v_3(\text{F}_{1u})\text{PtF}_6^-$	643 vs	$v_3(\text{F}_{1u})\text{PtF}_6^-$
1053 s	1054 (2.0)	$v_1(\text{A}_1)\text{ClO}_2^+$	1240	$v_2 + v_3(\text{F}_{1u} + \text{F}_{2u})\text{PtF}_6^-$	630 sh	$v_1(\text{A}_{1g})\text{PtF}_6^-$
1049 s			1216	$v_2 + v_4(\text{F}_{1u} + \text{F}_{2u})\text{ClF}_2^+$	564 s	$v_2(\text{E}_g)\text{PtF}_6^-$
890 s		$v_3(\text{F}_{1u})\text{ClF}_2^+$	1160	$v_1 + v_2(\text{A}_1)\text{ClF}_2^+$	564 s	$v_2(\text{E}_g)\text{PtF}_6^-$
	679 (0.5)	$v_1(\text{A}_{1g})\text{ClF}_2^+$	890	$v_3(\text{F}_{1u})\text{ClF}_2^+$	508 s	$v_3(\text{A}^+)\text{ClF}_2\text{O}^+$
640	vs	$v_3(\text{F}_{1u})\text{PtF}_6^-$	799 vs	799 (1.3) $v_3(\text{B}_1)\text{ClF}_2^+$	491 ns	$v_6(\text{A}^+)\text{ClF}_2\text{O}^+$
620	618 (3.1)		789 vs	788 (3.0) $v_1(\text{A}_1)\text{ClF}_2^+$	386 ns	$v_6(\text{A}^+)\text{ClF}_2\text{O}^+$
	644 (10)	$v_1(\text{A}_{1g})\text{PtF}_6^-$	784	784 (1) $v_2 + v_6(\text{F}_{1u} + \text{F}_{2u})\text{PtF}_6^-$	366 ns	$v_6(\text{A}^+)\text{ClF}_2\text{O}^+$
580 ns	569 (1.8)	$v_2(\text{E}_g)\text{PtF}_6^-$	704 (0+)		280 (0.3)	$v_6(\text{F}_{1u})\text{PtF}_6^-$
552 s	554 (2.5)		679 (3.0)	$v_1(\text{A}_{1g})\text{ClF}_2^+$	230 (7.9)	$v_3(\text{F}_{2g})\text{PtF}_6^-$
516 s	510 (0.6)	$v_2(\text{A}_1)\text{ClO}_2^+ + v_5(\text{F}_{2g})\text{ClF}_2^+$	658 vs, br	661 (0+) $v_3(\text{F}_{1u})\text{PtF}_6^-$	140 (0.3)	Lattice
	249 (4.5)	$v_5(\text{F}_{2g})\text{PtF}_6^-$	651 (2.5)	639 (19) $v_1(\text{A}_{1g})\text{PtF}_6^-$	115 (0.2)	Vibrations
	185 (0.2)	$v_6(\text{F}_{2u})\text{PtF}_6^-$	630 sh	630 $v_2(\text{E}_g)\text{ClF}_2^+$	58 (1.0)	
130 (0.1)		Lattice Vibrations	585 s, br	582 (0.8) $v_2(\text{E}_g)\text{PtF}_6^-$		
90 (1.6)			578	561 (3.1) $v_2(\text{E}_g)\text{ClF}_2^+$		
			510 v, sh	513 (0.3) $v_3(\text{F}_{2g})\text{ClF}_2^+$		
			478 v, sh			
			382 s	381 (0.2) $v_2(\text{A}_1)\text{ClF}_2^+$		
			376 sh			
			304 s	300 (0.5) $v_4(\text{F}_{1u})\text{PtF}_6^-$		
			265 s	282 (0.2) $v_6(\text{F}_{1u})\text{PtF}_6^-$		
			249 (3.2)			
			236 sh	$v_5(\text{F}_{2g})\text{PtF}_6^-$		
			229 (2.5)			
			170 (0.3)	$v_6(\text{F}_{2u})\text{PtF}_6^-$		
			101 (0.0)			
			72 (0.3)			
			54 (1.8)			
			42 (3.6)			
			26 (0.4)			
				Lattice		
				Vibrations		

ASSIGNMENT - RAMAN INTENSITIES ARE UNCORRECTED

ClF <sub>3</sub> O <sup>+</sup> PtF <sub>6</sub> <sup>-</sup>		ClF <sub>4</sub> <sup>+</sup> , ClF <sub>5</sub> <sup>+</sup> PtF <sub>6</sub> <sup>-</sup>		ClO <sub>2</sub> <sup>+</sup> IrF <sub>6</sub> <sup>-</sup>	
Frequency, cm <sup>-1</sup> IR	Assignment for ClF <sub>3</sub> O <sup>+</sup> in C <sub>3</sub> , for PtF <sub>6</sub> <sup>-</sup> in O <sub>h</sub>	Obsd Frequency, cm <sup>-1</sup> IR	Assignment for ClF <sub>4</sub> <sup>+</sup> in C <sub>2v</sub> , for ClF <sub>5</sub> <sup>+</sup> and PtF <sub>6</sub> <sup>-</sup> in O <sub>h</sub>	Obsd Frequency, cm <sup>-1</sup> IR	Assignment for ClO <sub>2</sub> <sup>+</sup> in C <sub>2v</sub> , for IrF <sub>6</sub> <sup>-</sup> in O <sub>h</sub>
96 1324 (0.6)	$v_1(A')$ ClF <sub>3</sub> O <sup>+</sup>	1560 w	$v_1 + v_3(F_{1u})$ ClF <sub>6</sub> <sup>-</sup>	1300 vs	1301 (0.6) $v_3(B_1)$ ClO <sub>2</sub> <sup>+</sup>
99 1311 (0.2)		1515 w	$v_2 + v_3(F_{1u} + F_{2u})$ ClF <sub>6</sub> <sup>-</sup>	1206 s.	1287 (0.2) $v_1(A_1)$ ClO <sub>2</sub> <sup>+</sup>
8 737 (2.7)	$v_2(A')$ ClF <sub>3</sub> O <sup>+</sup>	1200 w, br	$v_2 + v_3(F_{1u} + F_{2u})$ PtF <sub>6</sub> <sup>-</sup>	1057 s	1057 (4.1) $v_1(A_1)$ ClO <sub>2</sub> <sup>+</sup>
8 705 (6.8)	$v_3(A'')$ ClF <sub>3</sub> O <sup>+</sup>	890 vs	$v_3(F_{1u})$ ClF <sub>6</sub> <sup>-</sup>	670 (10)	$v_1(A_{1g})$ IrF <sub>6</sub> <sup>-</sup>
9 656 (4.2)	$v_3(F_{1u})$ PtF <sub>6</sub> <sup>-</sup>	878 sh		640 vs, br	613 (0.9) $v_3(F_{1u})$ IrF <sub>6</sub> <sup>-</sup>
9 630 (1.0)	$v_1(A_{1g})$ PtF <sub>6</sub> <sup>-</sup>	785 vs	$v_3(B_2), v_1(A_1), v_6(B_1)$ ClF <sub>6</sub> <sup>-</sup>	561 (2.5)	$v_2(E_g)$ IrF <sub>6</sub> <sup>-</sup>
8 575 sh	$v_2(E_g)$ PtF <sub>6</sub> <sup>-</sup>	720 vw	$v_3 + v_6(F_{1u} + F_{2u})$ PtF <sub>6</sub> <sup>-</sup>	549 (4.8)	
8 564 (2.0)	$v_2(E_g)$ PtF <sub>6</sub> <sup>-</sup>	670 - vs	$v_3(F_{1u})$ PtF <sub>6</sub> <sup>-</sup>	518 s	519 (1.1) $v_2(A_1)$ ClO <sub>2</sub> <sup>+</sup>
8 506 (0.5)	$v_3(A'')$ ClF <sub>3</sub> O <sup>+</sup>	620 -		279 m	
9 461 (0.7)	$v_6(A'')$ ClF <sub>3</sub> O <sup>+</sup>	580 m	$v_2(E_g)$ PtF <sub>6</sub> <sup>-</sup>	258 s	$v_6(F_{1u})$ IrF <sub>6</sub> <sup>-</sup>
9 366 (0.2)	$v_4(A')$ ClF <sub>3</sub> O <sup>+</sup>	572 m	$v_2(A_1)$ ClF <sub>6</sub> <sup>-</sup>	240 (0.5)	$v_5(F_{2g})$ IrF <sub>6</sub> <sup>-</sup>
260 (0.3)	$v_4(F_{1u})$ PtF <sub>6</sub> <sup>-</sup>	551 sh	$v_7(B_1)$ ClF <sub>6</sub> <sup>-</sup>	185 (0.5)	$v_6(F_{2u})$ IrF <sub>6</sub> <sup>-</sup>
230 (7.9)	$v_3(F_{2g})$ PtF <sub>6</sub> <sup>-</sup>	545 s			
140 (0.3)		500 s	$v_3(A_1)$ ClF <sub>6</sub> <sup>-</sup>		
115 (0.2)	Lattice Vibrations	383 s	$v_9(B_2)$ ClF <sub>6</sub> <sup>-</sup>		
58 (1.0)		281 sh	$v_4(F_{1u})$ PtF <sub>6</sub> <sup>-</sup>		
		271 s			

octahedral structure has been established beyond doubt by  $^{19}\text{F}$  nmr spectroscopy<sup>3</sup>, were made on the basis of the following arguments. For octahedral  $\text{ClF}_6^+$ , we would expect ideally six normal modes of vibration which are classified as  $A_{1g} + E_g + 2F_{1u} + F_{2g} + F_{2u}$ . Of these, only the two  $F_{1u}$  modes will be infrared active, while only the  $A_{1g}$ ,  $E_g$ , and  $F_{2g}$  modes will be Raman active, assuming no other solid state effects such as site symmetry lowering or slight distortion of the octahedron. Three different salts containing  $\text{ClF}_6^+ \text{PtF}_6^-$  have been studied. In addition to  $\text{ClF}_6^+$ , they contain either the  $\text{ClO}_2^+$ , or the  $\text{ClF}_2^+$ , or the  $\text{ClF}_4^+$  cation. All three salts show a strong infrared absorption at  $890 \text{ cm}^{-1}$ . The frequency of this band is higher than that of any known ClF fundamental vibration and is assigned to the antisymmetric stretching vibration,  $\nu_3 (F_{1u})$  of  $\text{ClF}_6^+$ . This assignment is supported by the following observation. In all three salts, the  $890 \text{ cm}^{-1}$  band shows a pronounced shoulder at  $877 \text{ cm}^{-1}$ . The observed frequency difference of about  $13 \text{ cm}^{-1}$  is in good agreement with the  $^{35}\text{Cl} - ^{37}\text{Cl}$  isotopic shift value of  $12.5 \text{ cm}^{-1}$  computed for octahedral  $\text{ClF}_6^+$ , assuming 100-percent characteristic modes. Of the remaining unassigned bands, the second highest frequency belongs to a relatively intense Raman line at  $679 \text{ cm}^{-1}$ . Clearly, this line must be due to the totally symmetric stretching mode,  $\nu_1 (A_{1g})$ . The Raman spectrum of  $\text{ClF}_2^+$ ,  $\text{ClF}_6^+ \text{PtF}_6^-$  (trace d, Figure 2) shows a band at  $513 \text{ cm}^{-1}$ . It has the same frequency as the  $\text{ClO}_2^+$  deformation mode but cannot be due to  $\text{ClO}_2^+$  since there is no evidence for its more intense  $\nu_1 (A_1)$  mode at about  $1050 \text{ cm}^{-1}$ . The  $513 \text{ cm}^{-1}$  band might be assigned to either  $\nu_2 (E_g)$  or  $\nu_5 (F_{2g})$  of  $\text{ClF}_6^+$ .

It has previously been shown that the vibrational spectra of  $\text{ClO}_2^+ {^{27}}$ ,  $\text{ClF}_2^0 {^{31}}$ ,  $\text{ClF}_2^0 {^{4,28}}$ ,  $\text{ClF}_5 {^{34}}$ , and  $\text{ClF}_4 {^{33}}$  closely resemble those of isoelectronic  $\text{SO}_2$ ,  $\text{SF}_2^0$ ,  $\text{SF}_2^0 {^{2}}$ ,  $\text{SF}_5^-$ , and  $\text{SF}_4$ , respectively. A similar relationship might be expected for the isoelectronic pair  $\text{ClF}_6^+ - \text{SF}_6^-$  (see Table II). Comparison with the vibrations

spectrum of  $\text{SF}_6$ <sup>35,36</sup> suggests that the  $513 \text{ cm}^{-1}$  band is due to  $\nu_5 (\text{F}_{2g})$ . This is further supported by the absence of another band below  $513 \text{ cm}^{-1}$ , which might be assigned to this mode and by the observed combination bands in the infrared spectrum. Generally, octahedral species exhibit two relatively intense combination bands in the infrared spectrum due to  $\nu_1 + \nu_3$  and  $\nu_2 + \nu_3$ . For  $\text{ClF}_6^+$ , two bands were observed at about  $1560$  and  $1515 \text{ cm}^{-1}$ , respectively. The  $1560 \text{ cm}^{-1}$  band represents  $\nu_1 + \nu_3$  (computed frequency:  $1569 \text{ cm}^{-1}$ ). Assuming the  $1515 \text{ cm}^{-1}$  band to be due to  $\nu_2 + \nu_3$ , a value of  $625 \text{ cm}^{-1}$  can be assigned to  $\nu_2$ . Inspection of trace d of Figure 2 reveals a shoulder at  $630 \text{ cm}^{-1}$ , which is assigned to  $\nu_2 (\text{E}_g)$  of  $\text{ClF}_6^+$ . Since there is no indication in the infrared spectrum for a combination band at about  $1400 \text{ cm}^{-1}$  ( $890 + 513 = 1403$ ), the  $513 \text{ cm}^{-1}$  Raman band is assigned to  $\nu_5 (\text{F}_{2g})$ .

An alternate, although less probable, assignment is possible for  $\nu_2 (\text{E}_g)$  of  $\text{ClF}_6^+$ . Trace d of Figure 2 exhibits two bands at  $582$  and  $576 \text{ cm}^{-1}$ , respectively. We prefer, however, to attribute both of them to  $\nu_2 (\text{E}_g)$  of  $\text{PtF}_6^-$  since the  $\nu_5 (\text{F}_{2g})$   $\text{PtF}_6^-$  bands also show additional splitting and since again no evidence for the corresponding  $\nu_2 + \nu_3$  combination band can be found in the infrared spectrum at about  $1470 \text{ cm}^{-1}$ . Thus all the expected active modes have been assigned for  $\text{ClF}_6^+$  except for the antisymmetric deformation,  $\nu_4 (\text{F}_{1u})$ . This mode should be infrared active and by comparison with  $\text{SF}_6$ , occur in the range  $550 - 610 \text{ cm}^{-1}$ . A frequency of  $582 \text{ cm}^{-1}$  is tentatively assigned to  $\nu_4$  based on traces c, d, and e of Figure 1 and by comparison with the infrared spectrum of  $\text{ClF}_2^0 \text{PtF}_6^-$ <sup>22</sup>.

TABLE II  
Fundamental Vibrations of  $\text{ClF}_6^+$  Compared to Those of Isoelectronic  $\text{SF}_6$

$\text{ClF}_6^+$	$\text{SF}_6$ (a)	Assignment in Point Group $O_h$
679	769.4	$\nu_1 (A_{1g})$
630	639.5	$\nu_2 (E_g)$
890	947.9	$\nu_3 (F_{1u})$
582	614.5	$\nu_4 (F_{1u})$
513	522	$\nu_5 (F_{2g})$

(a) Data from Reference 35 and 36.

Force Constants. A modified valence force field was computed for  $\text{ClF}_6^+$  in order to obtain a more quantitative understanding of its relative bond strength. Except for the  $F_{1u}$  block, all the symmetry force constants are unique. The  $F_{1u}$  block is underdetermined since only two frequency values are available for the determination of three force constants. A third frequency value for the  $F_{1u}$  block might be obtained from the  $^{35}\text{Cl}$ - $^{37}\text{Cl}$  isotopic shifts which would allow the computation of a general valence force field. Unfortunately, the isotopic shift for  $\nu_3$  could not be determined with sufficient accuracy. Consequently, the usefulness of mathematical constraints, such as minimizing or maximizing the value of one of the symmetry force constants was tested for isoelectronic  $\text{SF}_6$ , for which a general valence force field has been reported<sup>37</sup>. It was found that the condition,  $F_{44} = \text{minimum}^{38}$ , is the best approximation to the general valence force field, though it yields too high a value for  $F_{34}$ , due to appreciable coupling of the bonds<sup>39</sup>. It also results in a rather large negative value (-0.269 mdyn/Å) for the stretch-stretch interaction constant,  $f_{rr}'$ , which is difficult to rationalize. Using the same condition for computing the force field of  $\text{ClF}_6^+$ , a comparable negative value (-0.297 mdyn/Å)

was obtained for  $f_{rr}'$  of  $\text{ClF}_6^+$ . Since for  $\text{SF}_6$  the GVFF value of  $f_{rr}'$  is essentially zero, we prefer for  $\text{ClF}_6^+$  the condition  $f_{rr}' = 0$ . The resulting force field is listed in Table III and compared to the GVFF values of  $\text{SF}_6$ <sup>37</sup>.

TABLE III

Symmetry and Internal Force Constants (mdyn/Å) of  $\text{ClF}_6^+$   
Computed for a Modified Valence Force Field Assuming  
 $f_{rr}' = 0$  and Using the Frequency Values of Table II. For  
Comparison the GVFF Values of  $\text{SF}_6$  are also Listed.

	$\text{ClF}_6^+$	$\text{SF}_6$
$F_{11}$	5.161	6.628
$F_{22}$	4.443	4.578
$F_{33}$	4.682	5.256
$F_{34}$	0.726	0.885
$F_{44}$	0.955	1.035
$F_{55}$	0.736	0.763
$f_r$	4.682	5.258
$f_{rr}'$	0.120	0.341
$f_{rr}''$	0	0.002
$f_{r\alpha} - f_{r\alpha}''$	0.363	0.443

The force constant of greatest interest is the stretching force constant,  $f_r$ . Its value is 4.7 mdyn/Å with a conservative uncertainty estimate of  $\pm 0.2$  mdyn/Å considering the uncertainties in the frequency of  $\nu_4$  ( $F_{1u}$ ) and in the approximating method used for the force constant computation. This value is comparable to those

of  $\text{ClF}_2^+$  (4.74 mdyn/Å)<sup>40</sup> and of the equatorial Cl-F bonds in  $\text{ClF}_4^+$  (4.59 mdyn/Å)<sup>33</sup>, but significantly higher than those of the remaining known chlorine fluorides. The high value of  $f_r$  in  $\text{ClF}_6^+$  can be explained to some extent by the formal positive charge which generally increases the stretching force constant values. It also suggests strong covalent contributions to the bonding. The high  $f_r$  value is entirely consistent with the high stability observed for the  $\text{ClF}_6^+$  salts and parallels the findings for the  $\text{NF}_4^+$  salts<sup>6-9</sup>. In both cases, comparison with the isoelectronic molecules  $\text{SF}_6$  and  $\text{CF}_4$ , respectively, suggested unusual stability, although it proved difficult to actually synthesize these salts. In particular, it appears that the synthesis of  $\text{ClF}_6^+$  requires an unusually powerful oxidative fluorinating agent such as  $\text{PtF}_6$ .

Since  $\nu_4$  ( $\text{F}_{1u}$ ) and  $\nu_6$  ( $\text{F}_{2u}$ ) have been observed for both  $\text{PtF}_6^-$  and  $\text{IrF}_6^-$ , a modified valence force field was also computed for these two anions assuming octahedral symmetry and  $F_{44} = \text{minimum}$ . For  $\text{PtF}_6^-$  and  $\text{IrF}_6^-$ , this extremal condition is expected to give a force field close to that of a GVFF owing to the large mass of the central atoms and the resulting weak coupling. The frequencies used for the computation are listed in Table IV, together with the resulting force constants. The value of  $f_r$  of  $\text{PtF}_6^-$  (3.89) is intermediate between those of  $\text{PtF}_6$  (4.46)<sup>41</sup> and  $\text{PtF}_6^{--}$  (3.42 mdyn/Å)<sup>41</sup> as expected on the basis of the increasing formal negative charge.

Summary. The successful synthesis of  $\text{ClF}_6^+$  and the evidence for the nonexistence of a stable  $\text{ClF}_7$  molecule and  $\text{ClF}_6^-$  anion<sup>14</sup> completes the series of possible binary chlorine fluoride molecules and ions. Table V summarizes the presently known species. The existence of  $\text{ClF}_6^+$  suggests the possibility of preparing  $\text{ClF}_5^0$  and efforts to synthesize this new oxyfluoride will be continued.

TABLE IV

Symmetry and Internal Force Constants (mdyn/Å) of  $\text{PtF}_6^-$  and  $\text{IrF}_6^-$  Computed for a Modified Valence Force Field Assuming  $F_{44}^-$  = Minimum

	$\text{PtF}_6^-$ (a)	$\text{IrF}_6^-$ (b)
$F_{11}$	4.613	5.025
$F_{22}$	3.573	3.510
$F_{33}$	3.870	3.861
$F_{34}$	0.100	0.101
$F_{44}$	0.308	0.307
$F_{55}$	0.161	0.172
$F_{66}$	0.181	0.192
$f_r$	3.894	3.940
$f_{rr}$	0.173	0.255
$f_{rr}'$	0.024	0.079
$f_{r\alpha} - f_{r\alpha}''$	0.050	0.051
$f_{\alpha\alpha} - f_{\alpha\alpha}'' + f_{\alpha\alpha}'''$	0.171	0.182
$f_{\alpha\alpha} - f_{\alpha\alpha}'' + f_{\alpha\alpha}'''$	-0.010	-0.010

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Frequencies Used:

(a)  $\nu_1 = 642$ ,  $\nu_2 = 565$ ,  $\nu_3 = 640$ ,  $\nu_4 = 270$ ,  $\nu_5 = 240$ ,  $\nu_6 = 180 \text{ cm}^{-1}$ .

(b)  $\nu_1 = 670$ ,  $\nu_2 = 560$ ,  $\nu_3 = 640$ ,  $\nu_4 = 270$ ,  $\nu_5 = 248$ ,  $\nu_6 = 185 \text{ cm}^{-1}$ .

TABLE V

Summary of Existing Binary Chlorine Fluorides. Nonexisting Species Are Given in Parentheses.

$\text{Cl}_2\text{F}^+$ (a)	$\text{ClF}$ (b)	$\text{ClF}_2^-$ (c)
$\text{ClF}_2^+$ (d)	$\text{ClF}_3$ (e)	$\text{ClF}_4^-$ (f)
$\text{ClF}_4^+$ (g)	$\text{ClF}_5$ (h)	$(\text{ClF}_6^-)$ (e)
$\text{ClF}_6^+$ (i)	$(\text{ClF}_7)$ (i)	$(\text{ClF}_8^-)$

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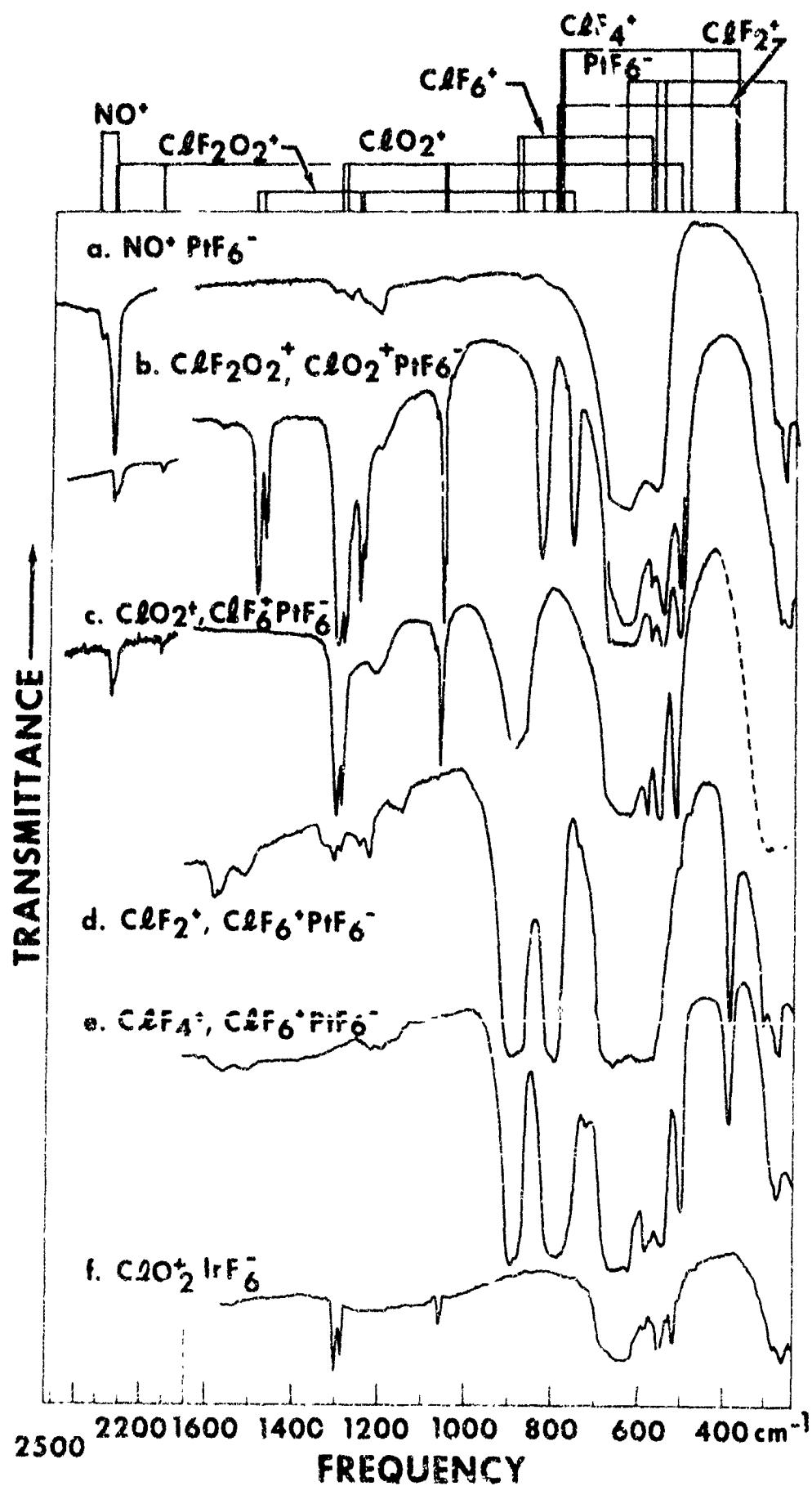
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Diagram Captions

Figure 1. Infrared spectra of the solid products obtained from the following reactions: trace a, displacement reaction between FNO and a mixture of  $\text{ClF}_2^+$  $\text{PtF}_6^-$  and  $\text{ClF}_6^+$  $\text{PtF}_6^-$ ; traces b and c,  $\text{FClO}_2 + \text{PtF}_6$  at 25 and  $-78^\circ$ , respectively; traces d and e,  $\text{ClF}_5$  and  $\text{PtF}_6$  using unfiltered and filtered uv radiation, respectively; trace f,  $\text{FClO}_2 + \text{IrF}_6$  at  $25^\circ$ . All spectra were recorded as pressed AgBr disks, except for trace c for which a AgCl disk was used.

Figure 2. Raman spectra of some of the solid products shown in Figure 1 using the same notations. All spectra were recorded for dry powders in glass melting point capillaries, using the  $6471 \text{ \AA}$  exciting line on a Cary Model 82.



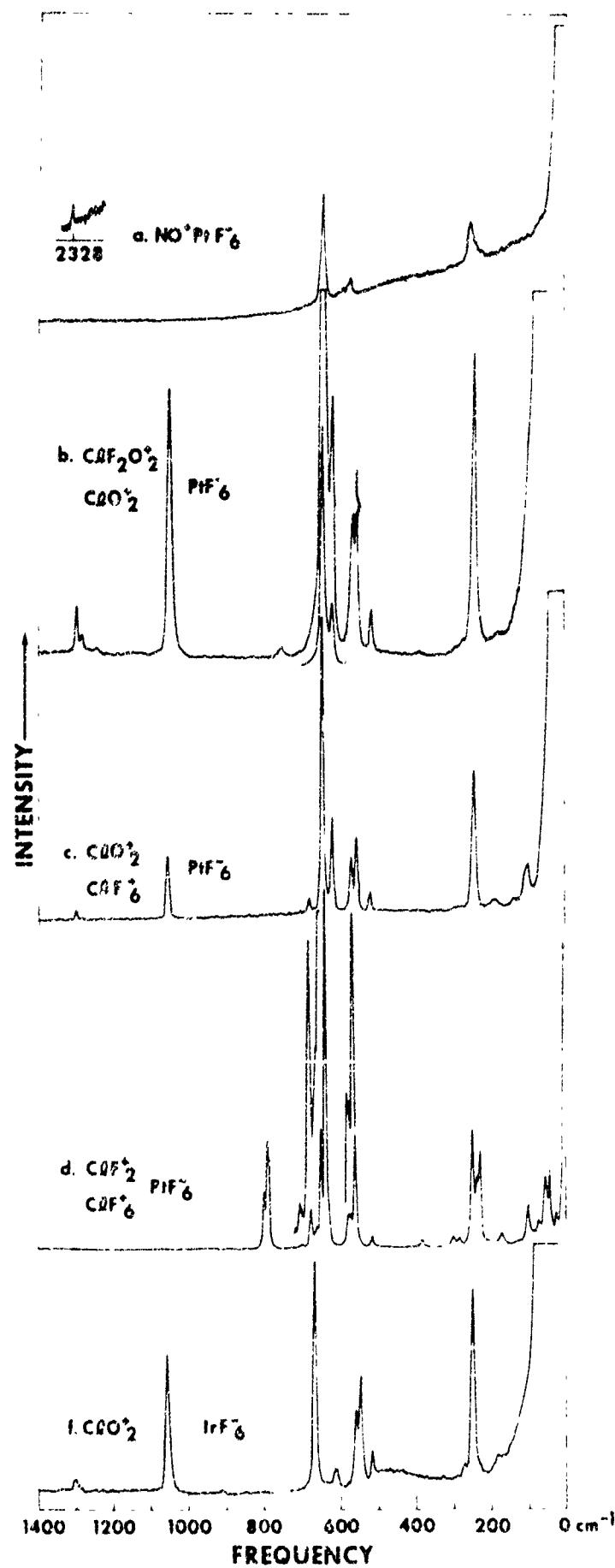


Figure 2.

120

On The Existence of Chlorine Oxide Pentafluoride [\*\*]

By Karl O. Christe, Richard D. Wilson, and Donald Pilipovich [\*]

The recent report by Zuechner and Glemser<sup>[1]</sup> on the synthesis of  $\text{ClF}_5\text{O}$  from the photolysis of  $\text{ClF}_5\text{-OF}_2$  mixtures prompted us to thoroughly study this system. Contrary to the previous report<sup>[1]</sup>, no evidence for the existence of  $\text{ClF}_5\text{O}$  could be obtained in the temperature range  $-78^\circ\text{C}$  to  $30^\circ\text{C}$ , using both unfiltered and Pyrex filtered uv radiation. All reactions were carried out in a stainless steel reactor equipped with a sapphire window. The progress of the reactions was periodically monitored by gas chromatography. At the end of an experiment, the products were also separated by fractional condensation, in a Teflon-stainless steel vacuum system and were characterized by vibrational spectroscopy. It was shown that in the  $\text{ClF}_5\text{-OF}_2$  system, when exposed to unfiltered uv radiation,  $\text{ClF}_5$  rapidly decomposes to  $\text{ClF}_3$  and  $\text{F}_2$  and, therefore, yields only the same products obtainable from the photolysis of  $\text{ClF}_3\text{-OF}_2$  mixtures.

The following properties reported by Zuechner and Glemser<sup>[1]</sup> for  $\text{ClF}_5\text{O}$  do not agree with the general trends observed for the remaining chlorine fluorides and oxyfluorides: i) nonvolatility at  $-78^\circ\text{C}$ , (ii) a  $^{19}\text{F}$  nmr resonance between  $-146$  and  $-103$  ppm relative to  $\text{CFCl}_3$ , and (iii) exchange broadening in the nmr spectrum even at  $-78^\circ\text{C}$ . For  $\text{ClF}_5\text{O}$ , we would expect (i) a volatility comparable to those of  $\text{ClF}_5$ <sup>[2]</sup> or  $\text{SF}_6$ <sup>[3]</sup>, (ii) an averaged  $^{19}\text{F}$  nmr chemical shift of about  $-390$  ppm<sup>[4]</sup>, and (iii) the absence of intramolecular exchange owing to chlorine having its maximum coordination number and no free valence electron pair and owing to the lack of a plausible exchange mechanism.

The only remaining piece of evidence presented<sup>[1]</sup> for  $\text{ClF}_5\text{O}$  is the presence of a low intensity fragment due to  $\text{ClF}_4\text{O}^-$  in the negative ion mass spectrum of the crude reaction product. We prefer to attribute this fragment to a recombination process in the mass spectrometer since a 52% peak was also reported for  $\text{F}_2^-$  which can form only by recombination. Furthermore, negative ion spectra frequently show species of higher mass than that of the parent molecule due to attachment of other atoms or groups<sup>[5]</sup>.

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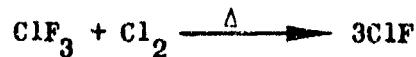
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## THE PREPARATION OF CHLORINE MONOFLUORIDE

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Chlorine monofluoride is a very vigorous and useful reagent which exhibits a diversity of reaction paths. Thus fluorinating, chlorinating, and chlorofluorinating reactions are well known (1) as well as amphoteric behavior in forming Lewis acid and base complexes (1, 2). Despite this broad utility, specific details regarding the synthesis of ClF are lacking. The experiments reported herein describe a simple, laboratory scale, procedure for the preparation of ClF.

Although ClF can be prepared from the elements (3), it is generally preferable to employ ClF<sub>3</sub> and Cl<sub>2</sub> according to the equation:



This reaction was first reported (4) by Schmitz and Schumacher. In their work and in later applications (5, 6) the reactions were carried out at temperatures in the range of 250 - 350°C and at unspecified pressures and/or times. Therefore, it appeared desirable to better define the most significant parameters, i.e., temperature, pressure, and time. The following table summarizes some of our typical results.

TABLE 1  
Reaction Data For 1.06 ClF<sub>3</sub> - 1.00 Cl<sub>2</sub>

Run No.	T <sup>o</sup> C	Max. Pressure psi	Time, hr.	ClF <sub>3</sub> Recovered	% Yield Purified ClF
1	120	160	65	Yes	65
2	150	200	18	Yes	79
3	150	620	18	No	95
4	180	375	5	No	92
5	180	670	6	Trace	92

From these experiments it is evident that a temperature of 120<sup>o</sup>C is too low for obtaining a high yield in a reasonable time. However, a temperature of 180<sup>o</sup>C, still much lower than those most often used, is quite satisfactory for producing complete reaction in a short time, over a broad pressure range. At 150<sup>o</sup>C a slightly higher yield was achieved, perhaps due to reduced wall reactions. The longer time required, 18 hr., is still a convenient overnight period. In all cases a 5-7 mole percent excess of ClF<sub>3</sub> was used to ensure sufficient material for the desired reaction since inevitably some fluorine is "lost" through formation of metal fluorides. These conditions have been successfully tested on a reaction scale of a few mmoles to about one mole of ClF.

Experimental

Commercial (The Matheson Co.) ClF<sub>3</sub> (98%) and Cl<sub>2</sub> (99.5%) were used without further purification. Stainless steel (304), single ended, high pressure (1800 psi) cylinders (Hoke, Inc.) were used together with stainless steel (316) valves (Hoke, Inc.) and bourdon tube gauges (The Matheson Co.). Clean, assembled

reactors were passivated with  $\text{ClF}_3$  at ambient temperature before use. Measured amounts of  $\text{ClF}_3$  and  $\text{Cl}_2$  were condensed into the cylinder held at  $-196^\circ\text{C}$ . After warming to ambient temperature, the loaded reactors were heated to the final reaction temperature in an oven or with heating tape. Because the temperature-pressure maximums employed were well below ratings for the equipment, small reactors could be placed completely (valve, gauge and all) and safely in an inexpensive drying oven set at the desired temperature. The heating cycle was conducted in an outdoor, pressure safe facility. On completion of the reaction, the contents of the cooled cylinders were separated by fractional condensation in a metal-Teflon vacuum line. A trap cooled to  $-142^\circ\text{C}$  (methylcyclopentane slush) was used to retain impurities such as  $\text{Cl}_2$ ,  $\text{ClF}_3$ , and  $\text{FCIO}_2$ , while the  $\text{ClF}$  was condensed in a trap held at  $-196^\circ\text{C}$ . The purity of the  $\text{ClF}$  was determined by gas chromatography (7) and its infra-red spectrum.

#### Acknowledgement

The authors are grateful to the Office of Naval Research, Power Branch, for support of this work and to Dr. K. O. Christe for helpful discussion.

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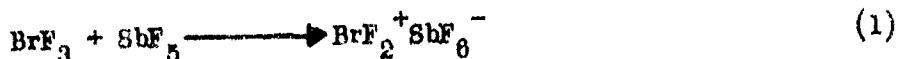
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On A New Synthesis of  $\text{NF}_4^+$  Salts and its Mechanistic Interpretation  
Involving A New and Exceptionally Powerful Oxidizing Species

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Complex fluoro cations are generally prepared through fluorine abstraction from the parent molecule by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus<sup>1</sup> for  $\text{BrF}_3$ :



In the case of  $\text{NF}_4^+$  salts, this approach was impossible since the parent molecule  $\text{NF}_5$  is unknown and unlikely to exist owing to the validity of the octet rule for first row elements such as nitrogen and fluorine. The synthesis of  $\text{NF}_4^+$  from  $\text{NF}_3$  and  $\text{F}^+$  is preempted by the fact that fluorine is the most electronegative element and, hence,  $\text{F}^+$  should be extremely difficult, if not impossible, to prepare by chemical means. In 1965, Christe and co-workers discovered<sup>2</sup> that  $\text{NF}_4^+$  salts can be prepared from  $\text{NF}_3$ ,  $\text{F}_2$ , and a strong Lewis acid in the presence of an activation energy source. Presently, three methods are known which are capable of producing  $\text{NF}_4^+$  salts. These are (1) glow discharge at low temperature<sup>3,4</sup>, (2) heating under high pressure<sup>5,6</sup>, and (3) bremsstrahlung at  $-196^{\circ}\text{C}$ <sup>7</sup>. In this note, we describe a fourth method, i.e., uv photolysis, which is capable of producing  $\text{NF}_4^+$  salts.

In addition to the great challenge which the preparation of  $\text{NF}_4^+$  salts presented to the synthetic chemist, the  $\text{NF}_4^+$  formation is of unusual interest from a mechanistic point of view. In view of the second and fourth methods of formation (see above), the originally suggested<sup>2</sup> mechanism cannot be considered satisfactory and a more plausible mechanism is offered. Based on the revised mechanism, we postulate a new intermediate of unusual oxidizing power comparable to that<sup>8</sup> of  $\text{PtF}_6$ .

### Experimental Section

Materials and Apparatus. The materials used in this work were manipulated in a well-passivated (with  $\text{ClF}_3$ ) 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 IF4Y). Pressures were measured with a Heise-Pourdon tube-type gauge ( $0 - 1500 \text{ mm} \pm 0.1\%$ ). Nitrogen trifluoride (Air Products),  $\text{BF}_3$  (The Matheson Company), and  $\text{AsF}_5$  (Ozark Mahoning Company) were purified by fractional condensation. Prior to its use, fluorine (Rocketdyne) was passed through a  $\text{NaF}$  trap to remove  $\text{HF}$  impurities. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box. The infrared spectra were recorded on a Perkin-Eimer Model 457 spectrophotometer as dry powders between  $\text{AgCl}$  windows in the form of pressed disks. The pressing operation was carried out using a Wilks mini pellet press. All reactions were carried out in a sapphire reaction tube brazed to a 304 stainless steel tube (Varian, Model CS-4250-3). This reactor had a volume of 23 ml. For the photolyses, unfiltered uv radiation from a Hanovia Model 616A high-pressure quartz mercury-vapor arc was used. In all reactions,  $\text{NF}_3$ ,  $\text{F}_2$ , and the corresponding Lewis acid were used in 1:1:1 mole ratios (2 mmol of each) resulting in an autogenous pressure of about 0.5 atmospheres.

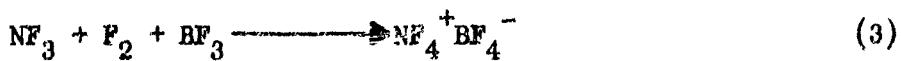
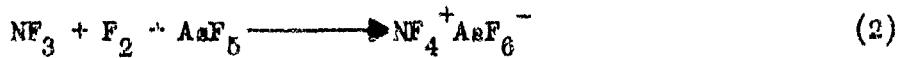
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Preparation of  $\text{NF}_4^+\text{AsF}_6^-$ . A mixture of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{AsF}_5$ , when kept for three days at  $25^\circ$  in a sapphire reactor in the dark, showed no detectable trace of solid formation. Upon exposing the sapphire section of the reactor to unfiltered uv radiation, clouds of suspended solid appeared within seconds inside the reactor resulting in an instant coating on the reactor walls. Continued exposure (for several days) of the reactor to uv radiation did not significantly increase the solid formation. After removal of the volatile reaction products, the weight gain of the reactor varied from 2 to 8 mg in several experiments. The solid residue was identified by vibrational spectroscopy<sup>9,10</sup> as  $\text{NF}_4^+\text{AsF}_6^-$  and in all cases did not show any detectable impurities.

Preparation of  $\text{NF}_4^+\text{BF}_4^-$ . The  $\text{NF}_3\text{-F}_2\text{-BF}_3$  reaction was carried out in the same way as described for  $\text{NF}_3\text{-F}_2\text{-AsF}_5$ . The reactants behaved similarly and the reaction rate decreased sharply with increasing solid deposition on the inside walls of the reactor. The yield of  $\text{NF}_4^+\text{BF}_4^-$  was between 1 and 2 mg. The infrared spectrum of the solid was in excellent agreement with that previously reported<sup>7</sup> for  $\text{NF}_4^+\text{BF}_4^-$ .

#### Results and Discussion

When gaseous mixtures of  $\text{NF}_3$ ,  $\text{F}_2$ , and the strong Lewis acids  $\text{AsF}_5$  or  $\text{BF}_3$  are exposed to unfiltered uv irradiation, the following rapid and reproducible reactions occur:



In all experiments, the yield of the  $\text{NF}_4^+$  salt was less than one percent. This low yield, however, appears not to be caused by a low reaction rate, but by deposition of the solid product on the reactor walls, thus preventing further irradiation of the reactants. Significant improvement of the yields should be possible by continuous removal of the deposits from the wall or the use of a more sophisticated flow system. However, efforts in this direction were beyond the scope of the present study. In view of the relatively low intensity of the uv lamp used in our experiments and the small diameter of the sapphire reactor, the observed high initial reaction rate strongly suggests a quantum yield larger than one, i.e., a chain reaction.

Taking all the presently available experimental data on the synthesis of  $\text{NF}_4^+$  compounds into consideration, additional conclusions concerning a plausible reaction mechanism can be reached. Based on the glow-discharge synthesis, we had originally invoked the intermediate formation of a  $\text{F}^+$  or  $\text{NF}_3^+$  cation<sup>2</sup>. Whereas these cations might indeed be produced under glow-discharge conditions, the high ionization potentials of  $\text{NF}_3$  (13.00 eV)<sup>11</sup>,  $\text{F}_2$  (15.69 eV)<sup>12</sup>, or  $\text{F}\cdot$  (17.44 eV)<sup>13</sup> preclude their formation in the uv photolysis, since the maximum energy available from the uv source does not exceed 7 eV. Even stronger evidence for an alternate mechanism stems from the thermal synthesis (method 2). Heating to about 120° cannot provide the activation energies required for the formation of  $\text{NF}_3^+$ ,  $\text{F}_2^+$ , or  $\text{F}^+$ . However, it has been found for the  $\text{Cl}_2\text{-F}_2$  dark reaction<sup>14,15</sup> that a temperature of about 120° is sufficient to dissociate some of the  $\text{F}_2$  into  $\text{F}\cdot$  radicals [ $D^0(\text{F}_2)$  is only 37.5 kcal mol<sup>-1</sup> = 1.82 eV]<sup>16</sup>. Inspite of the very low  $\text{F}\cdot$  atom concentrations expected at 120°, a chain reaction may result in relatively fast reaction rates. Based on these considerations and the observed fast initial reaction rate in the  $\text{NF}_3\text{-F}_2\text{-AsF}_5$  photolysis, it seems safe to postulate  $\text{F}_2$  dissociation as the first reaction step in the  $\text{NF}_4^+\text{AsF}_6^-$  synthesis:

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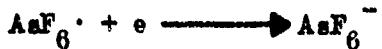
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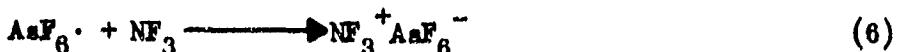
The next step could involve the reaction of  $F \cdot$  with either  $NF_3$  or  $AsF_5$ . Since the hypothetical  $NF_4 \cdot$  containing only first row elements would violate the octet rule, its formation is very unlikely. Therefore, the second step should be:



This step appears plausible since  $AsF_5$  generally acts as an excellent acceptor molecule and changes from a trigonal bipyramidal to an energetically more favorable octahedral  $AsF_6 \cdot$  configuration. The  $AsF_6 \cdot$  radical is pseudo-isoelectronic with  $SF_3^+$  and, hence, a rough estimate for the exothermicity of the reaction



can be obtained from the known<sup>17</sup> photoionization threshold of  $AsF_6^-$  (15.29 eV). This high value strongly suggests that the  $AsF_6 \cdot$  radical is the only likely intermediate capable of oxidizing  $NF_3$ , which has a first ionization potential of 12.00 eV.<sup>11</sup> Consequently, the third reaction step in the  $NF_4^+AsF_6^-$  formation should be:



In order to maintain a chain reaction, the  $NF_3^+ AsF_6^-$  could react with  $F_2$ , according to:



A crude estimate of the bond energy changes involved in this step can again be obtained by comparison between the isoelectromic species:



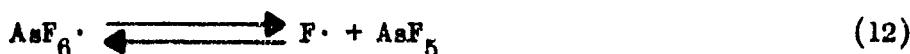
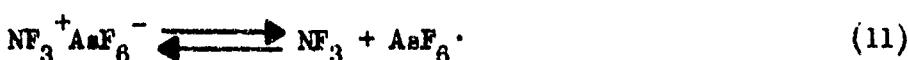
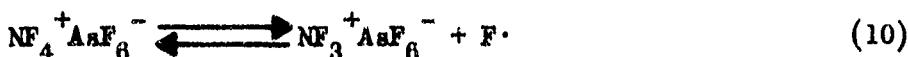
and



Since the  $\text{CF}_3\text{-F}$  bond energy ( $139.4 \text{ kcal mol}^{-1}$ )<sup>18</sup> is considerably higher than that of the  $\text{F-F}$  bond ( $37.5 \text{ kcal mol}^{-1}$ )<sup>18</sup>, reaction (7) should also be exothermic. Chain termination steps could occur by combination of any two of the radicals involved in this mechanism. The overall sequence, equations (4), (5), (6), and (7) appear to be a very plausible mechanism requiring only a low activation energy for (4) in excellent agreement with the experimental observations.

Solomon and co-workers have studied<sup>19</sup> the kinetics of the thermal decomposition of  $\text{NF}_4^+\text{AsF}_6^-$  to  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{AsF}_5$  in the temperature range 175 to 222° at low pressure. Since Tolberg et al. have shown<sup>5</sup> that  $\text{NF}_4^+\text{AsF}_6^-$  can be formed in this temperature range from  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{AsF}_5$  under high pressure, reversibility of these reactions is indicated. Consequently, the  $\text{NF}_4^+\text{AsF}_6^-$  formation mechanism should allow us also to better understand the thermal decomposition. Solomon et al. observed<sup>19</sup> that both  $\text{NF}_3$  and  $\text{AsF}_5$  inhibit the decomposition reaction and suggest that the decomposition mechanism involves the reversible dissociation of the solid to  $\text{NF}_5$  and  $\text{AsF}_5$ , followed by the irreversible decomposition of  $\text{NF}_5$  as the rate determining step. However, the observed fractional-order kinetics could not be explained by an elementary reaction mechanism. The mechanism, suggested<sup>19</sup> by Solomon and co-workers has several shortcomings. In our opinion, the most serious ones are (1)  $\text{NF}_5$  violates the octet rule which is strictly valid for first row elements. Promotion of nitrogen electrons to the 3s level would result

in a prohibitively large activation energy for the  $\text{NF}_5^-$  formation; (2) the  $\text{NF}_4^+\text{AsF}_6^-$  formation and decomposition appear to be reversible; and (3) the inhibition of the  $\text{NF}_4^+\text{AsF}_6^-$  decomposition by  $\text{NF}_3$  addition suggests that the steps involving  $\text{NF}_3$  cannot be irreversible. For these reasons and by analogy with the mechanism discussed above for the  $\text{NF}_4^+\text{AsF}_6^-$  formation, a more plausible decomposition mechanism would be:



Because the steady-state F atom concentration would be determined by a number of reactions, including the reverse of reaction (7), a very complex rate expression might be expected. The recombination of F atoms could occur either homogeneously via a three-body collision or heterogeneously. The inhibiting effects of  $\text{NF}_3$  and  $\text{AsF}_5$  could result from the reduction of the steady-state F atom concentration caused by the shifting of the equilibria (10), (11), and (12) to the left.

The postulate of an  $\text{AsF}_6\cdot$  radical intermediate which can act as a powerful oxidizer, could also explain the following two previously reported<sup>20-22</sup> and highly unusual reactions.



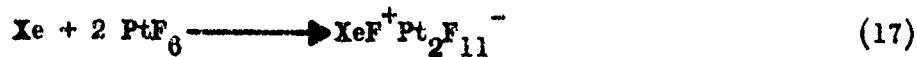
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Both reactions proceed again under very mild conditions, resulting in the oxidation of two species,  $O_2$  and  $Xe$ , with very high first ionization potentials of 12.06 and 12.13 eV, respectively. Reactions (14) and (15) are directly comparable to the following known<sup>8,23,24</sup>  $PtF_6^-$  reactions:



and



This analogy suggests that the oxidizing power of a Lewis acid- $F\cdot$  radical, such as  $AsF_6\cdot$ , is comparable to that of  $PtF_6^-$ , which is one of the strongest oxidizing fluorinators<sup>8</sup> known. The applicability of the Lewis acid-activated  $F_2$  system, however, seems to be limited to starting materials which themselves do not form stable adducts with the Lewis acid. The given examples demonstrate that the oxidizing power of fluorine can be promoted significantly by the simultaneous use of a strong Lewis acid and an energy source promoting dissociation of  $F_2$  into  $F\cdot$  atoms. Consequently, many reactions previously requiring the use of the prohibitively expensive  $PtF_6^-$  may now be carried out at a reasonable expense by the use of Lewis acid-promoted activated fluorine.

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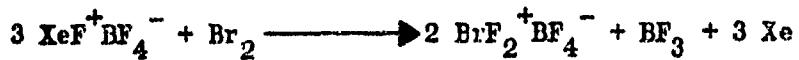
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ON THE REACTION OF  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$  WITH XENON

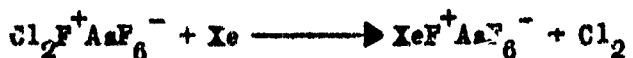
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In the presence of strong Lewis acids,  $\text{XeF}_2$  can act as a powerful fluorinating oxidizer (1,2). For example, it can fluorinate  $\text{Br}_2$  or  $\text{I}_2$  (3) resulting in the formation of  $\text{BrF}_3$  and  $\text{IF}_5$ , respectively, as shown by the following idealized equation:



followed by dissociation of the thermally unstable  $\text{BrF}_2^+\text{BF}_4^-$  complex to  $\text{BrF}_3$  and  $\text{BF}_3$  (4). However, to our knowledge, no example has been reported for the reverse reaction of this type, i.e., the oxidative fluorination of Xe by a halogen fluoride under mild conditions. Furthermore, previous studies have shown that both  $\text{ClF}$  (5) and  $\text{ClF}_3$  (6) do not interact with Xe.

We have now found that the addition of a Lewis acid to  $\text{ClF}$ , which causes  $\text{Cl}_2\text{F}^+$  formation (7), also increases the oxidizing power of  $\text{ClF}$  significantly so that it can fluorinate Xe according to:



followed by the known (8) reaction:



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These results suggest that the oxidizing power of cations decreases in the following order,  $\text{Cl}_2\text{F}^+ > \text{XeF}^+$  or  $\text{Xe}_2\text{F}_3^+ > \text{BrF}_2^+$ , and that the enhancement of the oxidizing power of an amphoteric molecule by the addition of a strong Lewis acid is not limited to  $\text{XeF}_2$  but is probably quite general. Furthermore, the fact that  $\text{ClF}$  is pseudo-isoelectronic with  $\text{XeF}^+$  but acts as a rather mild fluorinating oxidizer, indicates that a specific valence electron configuration is not the main cause for unusual oxidizing power. Rather, it appears that cation formation, i.e., a formal positive charge, is more important.

#### Experimental Section

Xenon,  $\text{ClF}$ , and  $\text{AsF}_5$  (2.09 mmol each) were combined at  $-196^\circ$  in a passivated (with  $\text{ClF}_3$ ) 25 ml sapphire-stainless steel reaction tube. The mixture was allowed to warm up to  $25^\circ$  and was kept at this temperature for one hour. The mixture was recooled to  $-196^\circ$  and did not show the presence of any noncondensable material. After removal of the products volatile at  $25^\circ$  by pumping, a white solid residue (83 mg) was obtained. The volatile material was condensed back into the reactor at  $-196^\circ$ . The contents were kept at  $-80^\circ$  for 1.5 hours. The reactor was allowed to warm to  $25^\circ$  and the volatile products were separated by fractional condensation. They consisted of  $\text{Xe}$  (1.68 mmol) and a mixture of  $\text{ClF}$ ,  $\text{Cl}_2$ , and  $\text{AsF}_5$  (total of 3 mmol) which could not be separated completely by fractional condensation owing to partial formation of the known  $\text{Cl}_2\text{F}^+\text{AsF}_6^-$  (7) and  $\text{Cl}_3^+\text{AsF}_6^-$  (9) adducts. The white solid residue (157 mg) showed the vibrational spectrum and x-ray powder diffraction pattern characteristic (10) for monoclinic  $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$ . The latter probably formed from the original  $\text{XeF}^+\text{AsF}_6^-$  (as indicated by the material balance) by loss of  $\text{AsF}_5$  during sample preparation in the glove box (8). Previous reports (8,11) on the infrared

spectrum and x-ray powder pattern diverge. Our data are in excellent agreement with the data of Bartlett et al. (8), but disagree with those reported by Binenboym et al.(11).

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On Halogen Pentafluoride-Lewis Acid Adducts<sup>1</sup>

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Abstract

Vibrational spectra have been recorded for the known adducts,  $\text{ClF}_5 \cdot \text{AsF}_5$ ,  $\text{ClF}_5 \cdot x \text{SbF}_5$  ( $x=1.08$  and  $1.36$ ),  $\text{BrF}_5 \cdot 2\text{SbF}_5$ , and  $\text{IF}_5 \cdot \text{SbF}_5$ . Furthermore, the new adduct,  $\text{BrF}_5 \cdot \text{AsF}_5$ , has been prepared. It is marginally stable at  $-95^\circ$ . The spectra of the  $\text{ClF}_5$  adducts are consistent with predominantly ionic structures containing the  $\text{ClF}_4^+$  cation. The spectrum of  $\text{ClF}_4^+$  is very similar to that of isoelectronic  $\text{SF}_4$  thus indicating a pseudo-trigonal bipyramidal structure of symmetry  $C_{2v}$ . All fundamentals have been assigned and a valence force field has been computed for  $\text{ClF}_4^+$ . The vibrational spectra of  $\text{IF}_5 \cdot \text{SbF}_5$  and  $\text{BrF}_5 \cdot 2\text{SbF}_5$  are compatible with the predominantly ionic structures,  $\text{IF}_4^+ \text{SbF}_6^-$  and  $\text{BrF}_4^+ \text{Sb}_2\text{F}_{11}^-$ , respectively, established by x-ray diffraction data. Tentative assignments are given for  $\text{BrF}_4^+$  and  $\text{IF}_4^+$ . The  $^{19}\text{F}$ nmr spectra of  $\text{BrF}_5 \cdot 2\text{SbF}_5$  and  $\text{IF}_5 \cdot \text{SbF}_5$  in HF solution are also reported.

## Introduction

Halogen fluorides exhibit amphoteric character. By combining with strong Lewis acids, they can form cations containing one  $F^-$  ion less than the parent molecule. In recent years these salts have received much attention, and numerous papers dealing with their syntheses and structures have been published<sup>2</sup>. Whereas the structures of the halogen mono-, tri-, and heptafluoride adducts are reasonably well established, much less is known about the complexes of the halogen pentafluorides.

Chlorine pentafluoride combines with Lewis acids such as  $AsF_5$ ,<sup>3</sup>  $SbF_5$ ,<sup>3,4</sup> and  $PtF_5$ .<sup>5,6</sup> Ionic structures containing the  $ClF_4^+$  cation were suggested,<sup>3,5</sup> however, no supporting data were presented. Recently, the  $^{19}F$  nmr spectrum of  $ClF_5 \cdot 1.36 SbF_5$  in  $HF-AsF_5$  solution was studied<sup>7</sup>. The observation of two resonances of equal intensity at low field is strong evidence for the presence of a  $ClF_4^+$  cation having a pseudo-trigonal bipyramidal structure of symmetry  $C_{2v}$ , analogous to that found<sup>8,9</sup> for isoelectronic  $SF_4$ .

Bromine pentafluoride forms with  $SbF_5$  the adduct,  $BrF_5 \cdot 2SbF_5$ <sup>10</sup>. A brief report on the  $^{19}F$  nmr spectrum of the solid and melt has been published<sup>11</sup> indicating the presence of two different kinds of fluorine ligands, however, the observed area ratio was in poor agreement with that expected for the postulated<sup>11</sup> structure  $BrF_4^+ Sb_2F_{11}^-$ . Recently, the crystal structure of  $BrF_5 \cdot 2SbF_5$  has been determined establishing<sup>12</sup> its predominantly ionic nature. After completion of our study<sup>1</sup>, Surles and coworkers have reported<sup>13</sup> the Raman spectra of  $BrF_4^+ Sb_2F_{11}^-$  and of  $BrF_5$  in  $SbF_5$  solution and proposed a tentative assignment for  $BrF_4^+$ . Solutions of  $BrF_5$  in  $SbF_5$  were shown<sup>13</sup> to be highly conductive suggesting an ionic formulation for the  $BrF_5 \cdot SbF_5$  adduct.

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Iodine pentafluoride forms 1:1 adducts with  $\text{SbF}_5^{14}$  and  $\text{PtF}_5^{15}$ . Recently, the crystal structure of  $\text{IF}_5 \cdot \text{SbF}_5$  has independently been studied by x-ray diffraction by two groups<sup>16,17</sup>. Unfortunately,  $\text{IF}_5 \cdot \text{SbF}_5$  tends to form twin crystals<sup>17</sup> thus rendering the structural determination somewhat difficult. Both groups suggest for  $\text{IF}_5 \cdot \text{SbF}_5$  a mainly ionic structure containing a distorted trigonal bipyramidal  $\text{IF}_4^+$  cation of symmetry  $C_{2v}$  and an  $\text{SbF}_6^-$  anion distorted from symmetry  $O_h$ . However, several interesting questions such as the difference in bond length between the axial and equatorial IF bonds remain unresolved. Shamir and Yaroslavsky have reported<sup>18</sup> in a preliminary communication the Raman spectra of a number of adducts including that of  $\text{IF}_5 \cdot \text{SbF}_5$ . However, their experimental data are incomplete and, therefore, their conclusions are little convincing.

### Experimental

Apparatus - The materials used in this work were manipulated either in a well passivated (with  $\text{ClF}_3$ ) 304 stainless steel vacuum system equipped with Teflon FEP U-traps or in the dry nitrogen atmosphere of a glove box. Pressures were measured with a Heise Bourdon tube-type gage (0-1500 mm  $\pm$  0.1%).

The Raman spectra of the solids were recorded with a Spex Model 1400 spectrophotometer. The green (5145 Å) or the blue (4880 Å) line of a Coherent Radiation Lab. Model 52 Ar ion laser and the red (6328 Å) line of a Spectra-Physics Model 125 He-Ne laser were used as exciting lines. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or clear Teflon FEP or Kel-F capillaries (1 to 4 mm i.d.) were used as sample containers. For the capillaries the transverse viewing-transverse excitation technique was applied. The Raman spectra of the HF solutions were recorded on a Cary Model 83 spectrophotometer using the 4880 Å

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exciting line. The samples were contained in Teflon FEP capillaries which were also used for the  $^{19}\text{F}$  nmr spectra.

The infrared spectra of the solids were recorded on a Beckman Model IR-7 with CsI interchange and Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000-250  $\text{cm}^{-1}$  as dry powders between AgCl or AgBr plates or thin (2 mil) Teflon FEP sheet. Compensation for bands due to the Teflon FEP window material was achieved by placing an empty cell in the reference beam. Screw-cap metal cells with Teflon FEP gaskets were used as window holders. The low-temperature infrared spectrum of  $\text{ClF}_5 \cdot \text{AsF}_5$  was taken by preparing the complex on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex-glass, all windows being AgCl. Temperature cycling of the internal window in vacuo was essential to obtain spectra free of unreacted starting materials.

The  $^{19}\text{F}$  nmr spectra were recorded at 56.4 MHz on a Varian high-resolution nmr spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the sideband technique with an accuracy of  $\pm 1$  ppm relative to the external standard  $\text{CFCl}_3$ .

Preparation of the  $\text{ClF}_5$  Adducts - The purification of  $\text{ClF}_5$ ,  $\text{SbF}_5$ ,  $\text{AsF}_5$ , and HF and the preparation of the  $\text{ClF}_5$ ·Lewis acid adducts has previously been described<sup>3</sup>. Since the melting point and the composition of the  $\text{ClF}_5 \cdot \text{SbF}_5$  samples varied somewhat with the method of preparation, three different samples were investigated. Sample I had the composition  $\text{ClF}_5 \cdot 1.08 \text{ SbF}_5$  and showed first signs of melting at 88°. It was prepared by adding an  $\text{SbF}_5$ -HF solution to excess  $\text{ClF}_5$ . Sample II had the composition  $\text{ClF}_5 \cdot 1.36 \text{ SbF}_5$  and

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was prepared by combining  $SbF_5$  dissolved in HF with an excess of  $ClF_5$  at  $-196^\circ$  followed by warm up to  $25^\circ$  and removal of volatile material in vacuo. It showed first indications of partial melting at  $\sim 35^\circ$ . With increasing temperature, however, the sample solidified again showing the onset of a second melting at  $88^\circ$ . Sample III had the same composition as sample II and was prepared by treating a part of sample II with excess  $ClF_5$  in a Monel cylinder at  $50^\circ$  for 48 hours with agitation. It melted at about  $33^\circ$  to form a milky, highly viscous liquid. The synthesis of the  $ClF_4^+PtF_6^-$  and  $ClF_6^+PtF_6^-$  mixture has previously been described<sup>6</sup>.

Preparation of  $BrF_5 \cdot 2 SbF_5$  - Bromine pentafluoride (from The Matheson Company) was treated with  $F_2$  at ambient temperature until the material was colorless. It was purified by fractional condensation through two traps kept at  $-64$  and  $-55^\circ$ . The material retained in the  $-95^\circ$  trap showed no detectable impurities in the infrared spectrum.

Bromine pentafluoride (112.3 mmole) was condensed at  $-196^\circ$  into a passivated 100 ml Monel cylinder containing 68.8 mmole of  $SbF_5$ . The cylinder was heated for three days to  $120^\circ$ . Subsequently, unreacted  $BrF_5$  (78.3 mmole) was removed in vacuo at ambient temperature leaving behind a white, crystallinic solid. Consequently,  $BrF_5$  (34.0 mmole) had reacted with  $SbF_5$  (68.8 mmole) in a mole ratio of 1:2.02 producing the complex  $BrF_5 \cdot 2 SbF_5$ .

Preparation of  $BrF_5 \cdot AsF_5$  - Bromine pentafluoride (4.42 mmole) was combined with  $AsF_5$  (13.15 mmole) at  $-196^\circ$  in a Teflon FEP U-trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 1200 mm, the mixture was cooled again

to  $-196^{\circ}$ . This procedure was repeated several times until the reaction was complete. Unreacted  $\text{AsF}_5$  (8.77 mmole) was removed in vacuo at  $-95^{\circ}$  leaving behind a white solid which melted at higher temperature to form an almost colorless liquid. Prolonged pumping on the adduct at  $-95^{\circ}$  resulted in the removal of additional small amounts of  $\text{AsF}_5$  indicating that the adduct has a slight dissociation pressure even at  $-95^{\circ}$ . The infrared spectrum of the gas obtained by exhaustive dissociation of the solid showed  $\text{BrF}_5$  and  $\text{AsF}_5$  in a 1:1 mole ratio. Based on the above given material balance,  $\text{BrF}_5$  (4.42 mmole) had combined with  $\text{AsF}_5$  (4.38 mmole) in a mole ratio of 1:0.99 producing the complex  $\text{BrF}_5 \cdot \text{AsF}_5$ .

Preparation of  $\text{IF}_5 \cdot \text{SbF}_5$  - This product was prepared as previously described<sup>14</sup>. The material was a white, crystallinic solid. The material balance was as expected for a 1:1 adduct. Anal. Calcd. for  $\text{ISbF}_{10}$ : I, 28.9; Sb, 27.8; F, 43.3. Found: I, 29.4; Sb, 27.4; F, 43.0.

Liquid  $\text{IF}_5$  and gaseous  $\text{AsF}_5$  when combined at  $20^{\circ}$  with stirring did not form a stable adduct.

#### Results and Discussion

Syntheses and Properties - The preparation of the  $\text{ClF}_5$  adducts has previously been discussed<sup>3</sup>. In the  $\text{BrF}_5\text{-SbF}_5$  system we could not isolate a 1:1 adduct even when employing a large excess of  $\text{BrF}_5$  and temperatures above  $100^{\circ}$  in the synthesis. The  $\text{BrF}_5 \cdot 2 \text{ SbF}_5$  complex is a white crystallinic solid. It can be stored in Teflon FEP containers without appreciable decomposition. Exposure to small amounts of moisture or reactive surfaces produces a pink to deep red color due to the formation of  $\text{Br}_2^+$  salts<sup>2</sup>. Single crystals of

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$\text{BrF}_5 \cdot 2 \text{ SbF}_5$  can be readily grown by slow sublimation at temperatures slightly higher than ambient. The results of a single crystal x-ray diffraction study on  $\text{BrF}_5 \cdot 2 \text{ SbF}_5$  have been reported<sup>12</sup> elsewhere. With  $\text{AsF}_5$ , however,  $\text{BrF}_5$  does form a 1:1 adduct, but its thermal instability preempted its use for structural studies. Upon melting, the complex forms a colorless liquid. If impure  $\text{BrF}_5$  is used in the synthesis, the color of the liquid is an intense burgundy red indicating the presence of  $\text{Br}_2^+$  ions<sup>2</sup>. The fact that  $\text{AsF}_5$  and  $\text{SbF}_5$  combine with  $\text{BrF}_5$  in different mole ratios, might be explained by the pronounced tendency of  $\text{SbF}_5$  to form polymeric anions such as  $\text{Sb}_2\text{F}_{11}^-$ .

Our data obtained for  $\text{IF}_5 \cdot \text{SbF}_5$  confirm Woolf's reports<sup>14</sup>. Single crystals of  $\text{IF}_5 \cdot \text{SbF}_5$  were grown by slow sublimation at 40°. A single crystal x-ray diffraction study in our laboratory was discontinued when we learned about the work<sup>15</sup> of Baird and Giles. The fact that  $\text{AsF}_5$ , a weaker Lewis acid than  $\text{SbF}_5$ , does not form a stable adduct with  $\text{IF}_5$  is not surprising. As previously pointed out<sup>19</sup>, halogen pentafluorides possess an energetically favorable pseudo-octahedral structure and show little tendency to form the energetically less favorable pseudo-trigonal bipyramidal  $\text{XF}_4^+$  cations.

<sup>19</sup>F nmr Spectra - The <sup>19</sup>F nmr spectrum of  $\text{ClF}_5 \cdot 1.36 \text{ SbF}_5$  in acidified HF has previously been discussed<sup>7</sup>. The observation of two signals of equal intensity at -256 and -274 ppm, respectively, relative to  $\text{CFCl}_3$  below -60° is strong evidence for a  $\text{ClF}_4^+$  cation having two nonequivalent sets of two fluorine ligands<sup>7</sup>.

The  $^{19}\text{F}$  nmr spectrum of  $\text{BrF}_5 \cdot 2 \text{SbF}_5$  in HF or HF- $\text{AsF}_5$  solution showed between 20 and  $-80^\circ$  for the  $\text{BrF}$  part of the spectrum, a single resonance at  $-197$  ppm relative to external  $\text{CFCl}_3$ . In the HF-SbF region at  $20^\circ$  a very broad unresolved common peak centered at about 130 ppm was observed indicating fast exchange between the solvent and the anion. In more dilute solutions the  $\text{HF-Sb}_2\text{F}_{11}^-$  signal shifted to about 150 ppm and gained in relative intensity whereas the chemical shift of the  $\text{BrF}_4^+$  resonance remained constant. At lower temperatures ( $-60$  to  $-80^\circ$ ) the peak in the SbF region started to separate into several peaks at about 76, 93, 120, and 127 ppm. Whereas the identity of these peaks could not definitely be established, the chemical shifts of some of them are similar to those (93, 120, and 142 ppm) previously found for  $\text{Sb}_2\text{F}_{11}^-$  in HF solution<sup>20</sup>. The chemical shift of  $-197$  ppm found for  $\text{BrF}_4^+$  in HF differs significantly from that ( $-167$  ppm) reported by Meinert and Gross for the melt<sup>11</sup>. This discrepancy might be caused by the different environment.

A solution of  $\text{IF}_5 \cdot \text{SbF}_5$  in HF exhibited between 20 and  $-80^\circ$  only one signal at 133 ppm indicating rapid exchange between all species present. Acidification of the solvent with  $\text{AsF}_5$  did not influence the exchange rates sufficiently to cause a separation into individual signals.

The fact that the inter- and intra-molecular exchange rates decrease in the order  $\text{IF}_5 \cdot \text{SbF}_5 > \text{BrF}_5 \cdot 2 \text{SbF}_5 > \text{ClF}_5 \cdot \text{SbF}_5$  might be explained by the decreasing size and polarizability of the corresponding halogen pentafluorides.

Vibrational Spectra - The vibrational spectra of the halogen pentafluoride-Lewis acid adducts are shown in Figures 1 to 10. The infrared spectrum of the  $\text{ClF}_4^+\text{PtF}_6^-$  and  $\text{ClF}_6^+\text{PtF}_6^-$  mixture has previously been given<sup>6</sup> and, hence, is not shown here. The deserved frequencies are listed in Tables I and II.

Since the ionic nature and structure of the Lewis acid adducts of  $\text{ClF}_5$ ,  $\text{BrF}_5$  and  $\text{IF}_5$  has been established by x-ray diffraction,<sup>12,16,17</sup> nmr, and conductivity studies,<sup>13</sup> the discussion of their vibrational spectra can be kept relatively short. The main objective of this study is to demonstrate that the vibrational spectra are consistent with the known ionic structures, to define the principal bands of the  $\text{HalF}_4^+$  cations, and to examine the plausibility of the given assignments by comparison with the known spectra of isoelectronic chalcogen tetrafluorides and by force field computations.

Chlorine Pentafluoride Adducts - The infrared spectra of the  $\text{ClF}_5 \cdot x\text{SbF}_5$  adducts are relatively insensitive to changes in the  $\text{ClF}_5:\text{SbF}_5$  combining ratio owing to the relative broadness of the bands due to the Sb-F vibrations (see Figure 3). In the corresponding Raman spectra (Figures 1 and 2), however, slight changes in the composition of the adducts or in the procedures used for their preparation may cause significant changes. As expected, sample I, having the composition  $\text{ClF}_5 \cdot 1.08 \text{ SbF}_5$ , shows the simplest spectrum. With increasing  $\text{SbF}_5$  content and tempering features attributable to polymeric anions such as  $\text{Sb}_2\text{F}_{11}^-$  become more pronounced. Similarly, the low-temperature infrared spectrum of the  $\text{ClF}_5 \cdot \text{AsF}_5$  adduct (Figure 5) indicates the presence of the  $\text{As}_2\text{F}_{11}^-$  anion<sup>21,22</sup>. However, the  $\text{As}_2\text{F}_{11}^-$  anion is much less stable

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**TABLE I**  
**Vibrational Spectra of  $\text{ClF}_5 \cdot \text{Lewis Acid Adducts and Their Assignments Compared to That of } \text{SF}_4^+$**

$\text{SF}_4^+$ (gas)	$\text{R}_2^+$	Obsd. Frequencies ( $\text{cm}^{-1}$ ) and Relative Intensities <sup>b</sup>				Assignment (point group) <sup>c</sup>			
		$\text{ClF}_5 \cdot \text{SbF}_5^f$				$\text{ClF}_5 \cdot \text{SF}_5^g$			
		IR	RA	IR	RA (solid)	IR	RA (HF sol.)	IR	RA ( $\text{O}_{\text{h}}$ )
1744vw		1600vw, br							
1617vv		1390vw		1335w		822(2.5)		825sh	
1281w		830(0.5)		823s, sh		822(2.5)		825sh	
867s	865(0*)	827s	830(2.5)	803vs	802(10)	802(10)	802(10)	795vs	795vs
891s	888(9.0)	796vs	799(10)						
730vs	730(0+)			720vs	711(0.3)	669vs	670(0.5-2.5)		
				695(0.3)	671(8.0)	648vs	653(8.6)	656(8)	
				673ms	579(4)	579w	583(0.6-4)		
				584m	567(6.5)	566(5.5)	574(5.5)		
				576mw					
553m	553(10)	568w							$\nu_2(\text{A}_1)$
		553w							$\nu_2(\text{E})$
532as	532(4.0)	536mw	538(2.5)	535ms*	534(5)*	537(1)*	545s, br*		$\nu_7(\text{E})$
464vv	475(1.2)	511ms**	519(1)	510sh	515(0.2)	515(0+)	500s		$\nu_3(\text{A}_1)$
	414(0+)		473(1)		475(0.4)	475(0.4)			$\nu_5(\text{A}_1)$
353ms	350(0+)	395s		386m			383s	271s	$\nu_9(\text{B}_2)$
				399(0.6)	280s				$\nu_4(\text{E}_{\text{g}})$
				372(2.7)	279(1.4)	277(1)			$\nu_5(\text{E}_{\text{g}})$
				237(1.1)	235(0.5)	245sh			$\nu_4(\text{A}_1)$
226w	223(1.0)								

(a) Ref. 25; (b) Uncorrected Raman intensities; (c) Assignments for the anion bands are made assuming for simplicity octahedral symmetry, although in most cases the actual symmetry is expected to be lower than  $\text{O}_{\text{h}}$ ; (d) Ref. 23; (e) Ref. 24; (f) The low-temperature infrared spectrum indicates the presence of substantial amounts of  $\text{AsF}_5^+$ ; (g) The listed frequencies are those obtained for  $\text{ClF}_5 \cdot 1.08 \text{ SbF}_5$ ; The relative intensities of the 670, 583, and to a lesser extent of the 534  $\text{cm}^{-1}$  Raman band's varied, indicating different degrees of deviation of  $\text{SbF}_5^-$  from symmetry  $\text{O}_{\text{h}}$  or slight inhomogeneity of the sample; (h) Ref. 6.

TABLE II									
Vibrational Spectra of $\text{BrF}_5 \cdot 2\text{SbF}_5$ and $\text{IF}_5 \cdot \text{SbF}_5$ , Compared to Those of $\text{SeF}_4$ and $\text{TeF}_4$									
$\text{SeF}_4$		$\text{BrF}_5 \cdot 2\text{SbF}_5$		$\text{SbF}_4$		$\text{TeF}_4$		$\text{IF}_5 \cdot \text{SbF}_5$	
IR	RA	IR	RA	IR	RA	IR	RA	IR	RA
723s	724w, sh	730sh	[736sh (10)]	680sh	$\nu_8(\text{B}_2)$	695m	728sh	729(9)	704(10)
744ms	749vs, p	690vs	[723(10)]	704(2.4)	$\nu_8(\text{A}_1)$	682m	719m	720(1.6)	$\nu_1(\text{A}_1)$
622vs		655vs	650sh	[660(1.0)]	$\nu_6(\text{B}_1) + \text{Sb}_2\text{F}_{11}$ (1)	587s	691sh	693(2.2)	$\nu_8(\text{A}_2)$
			655sh	651(6.9)	$\text{Sb}_2\text{F}_{11}$		668sh	662(10)	$\text{SbF}_6$
				600sh	600sh		655vs	663(8)	
574s, p	606vw	616(4.8)	575(5)	$\nu_2(\text{A}_1)$			625m, sh	625(3)	$\nu_6(\text{A}_1)$
	568m	555(3.3)		$\text{Sb}_2\text{F}_{11}$	-	572vw		514(4)	$\nu_2(\text{A}_2)$
	540vw	545sh	540(1)	$\text{Sb}_2\text{F}_5\text{Sb}$			567w, sh	569(9)	$\text{SbF}_6$
	488as	490(1)	490(1)	$\nu_7(\text{B}_1)$			520vw, sh	521(1.5)	$\nu_7(\text{B}_1)$
405s,	400w	419s	335(0.5)	426(2)	$\nu_3(\text{A}_1)$	333w	388vw	335(0.8)	$\nu_3(\text{A}_2)$
	366m, p	369vw	359(0.5)	363(5)	$\nu_9(\text{B}_2)$	293vw	345w	341(0.4)	$\nu_9(\text{B}_1)$
			295(1)	280sh	$\text{Sb}_2\text{F}_{11}$	-	311w	316(0.2)	$\nu_9(\text{B}_2)$
			254(0.7)					299(0.9)	
			250(0.5)	235(0+)				285(0+)	$\text{SbF}_6$
160vw	162w, p		219(0.2)		$\nu_4(\text{A}_1)$	288m	280sh		
			15(1.5)		lattice mode	263vw	259(0.5)	250sh	
							151(0.4)		$\nu_4(\text{A}_1)$
							72(1)		lattice modes
							42(6)		

(a) Uncorrected Raman intensities; (b) Best values and assignments taken from Ref. 46-48  
 (c) Ref. 48

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than  $\text{Sb}_2\text{F}_{11}^-$  resulting in the facile removal of the second  $\text{AsF}_5$  molecule under the conditions<sup>3</sup> used for the synthesis of the Raman sample (1:1 adduct).

The vibrational assignments for  $\text{ClF}_4^+$  in point group  $C_{2v}$  (see Table I) were made by analogy with isoelectronic  $\text{SF}_4$ <sup>23-26</sup> and by comparison with the known spectra of compounds containing  $\text{AsF}_6^-$ <sup>21,27-29</sup>,  $\text{As}_2\text{F}_{11}^-$ <sup>21,22</sup>,  $\text{SbF}_6^-$  and  $\text{Sb}_2\text{F}_{11}^-$ <sup>20,28,30-33</sup> anions. In solids, the deviation of the spectra of these anions from those expected for the isolated octahedral ions is very common. It can be caused by effects such as site symmetry lowering, slight distortion of the octahedrons owing to crystal packing and anion-cation interaction, and the tendency to form polymeric anions. Unfortunately, the splittings, frequencies, and relative intensities of these bands strongly vary from compound to compound. Therefore, reliable assignments for the cations require the recording of spectra of adducts containing different anions or of solution spectra which usually show the bands characteristic of the unperturbed ions. Contrary to the highly symmetric octahedral  $\text{XF}_6^-$  anions, the  $\text{ClF}_4^+$  cation of symmetry  $C_{2v}$  should be very little influenced by solid state effects because it possesses already its maximum number (3n-6=9) of modes.

For the  $\text{ClF}_5$  adducts sufficient experimental data (see Table I) are available to distinguish the anion from the cation bands. As can be seen, the spectrum of  $\text{ClF}_4^+$  is very similar to that of isoelectronic  $\text{SF}_4$ <sup>23,24</sup>. This close resemblance is comparable to that found for the isoelectronic pairs,  $\text{SF}_2\text{O}^-$ ,  $\text{ClF}_2\text{O}^+$ ,<sup>34</sup>  $\text{SF}_2\text{O}_2\text{-ClF}_2\text{O}_2^+$ ,<sup>35</sup>  $\text{SF}_6^-$ - $\text{ClF}_6^+$ ,<sup>36</sup> and  $\text{SF}_5^-$ - $\text{ClF}_5$ ,<sup>37</sup> and, therefore, is not surprising. For  $\text{ClF}_4^+$ , the assignment to the individual modes was

made by analogy with  $SF_4$ . For  $SF_4$ , the assignment of Frey et al.<sup>25</sup> was used which was recently confirmed<sup>26</sup> by mean square amplitudes of vibration and force field computations.

In the spectra of the  $ClF_5$  adducts, nine bands are found which might be attributed to  $ClF_4^+$ . Of these, the intense infrared and Raman band at about  $800\text{ cm}^{-1}$  obviously represents the symmetric equatorial  $ClF_2$  stretching mode  $\nu_1$ . The moderately intense Raman and strong infrared band at about  $825\text{ cm}^{-1}$  then must be the antisymmetric equatorial stretch  $\nu_8$ . The symmetric axial stretch,  $\nu_2$ , falls within the range of the  $\nu_2$  anion bands, but is clearly identified by the strong Raman band at  $574\text{ cm}^{-1}$  in the HF solution. The antisymmetric axial stretching mode,  $\nu_6$ , should be of very high intensity in the infrared and of very low intensity in the Raman spectrum. By comparison with other pseudo-trigonal bipyramidal molecules such as  $ClF_3^{38}$  or  $ClF_3O_2^{39}$  it should occur above  $700\text{ cm}^{-1}$ . Since there is no additional yet unassigned strong infrared band above this frequency in all of the observed spectra, a coincidence with  $\nu_1$  must be assumed. The assignment of  $\nu_4$  and  $\nu_9$  to the bands at  $237$  and  $385\text{ cm}^{-1}$ , respectively, is clearcut and needs no further comment. This leaves us with three frequencies,  $537$ ,  $515$ , and  $475\text{ cm}^{-1}$ , for the assignment to  $\nu_7$ ,  $\nu_3$ , and  $\nu_5$ . Since the  $475\text{ cm}^{-1}$  band appears to be inactive in the infrared spectrum, we ascribe it to  $\nu_5$  which ideally should be forbidden in the infrared spectrum. Based on their relative Raman intensities, when compared to those of  $SF_4$ , we prefer to assign  $\nu_3$  and  $\nu_7$  to  $515$  and  $537\text{ cm}^{-1}$ , respectively. The assignments for  $\nu_3$ ,  $\nu_7$ , and  $\nu_5$  are somewhat tentative. However, a reassignment of these three deformational modes should owing to their similar frequencies, be of minor influence on the principal force constants.

Force Constants - The method used for the computation of the  $\text{ClF}_4^+$  force field has previously been described<sup>39</sup>. The following geometry was assumed for  $\text{ClF}_4^+$ ,  $r(\text{Cl}-\text{F}_{\text{eq}}) = 1.57$ ,  $R(\text{Cl}-\text{F}_{\text{ax}}) = 1.66\text{\AA}$ ,  $\alpha(\text{F}_{\text{ax}}\text{ClF}_{\text{eq}}) = 90^\circ$ ,  $\beta(\text{F}_{\text{eq}}\text{ClF}_{\text{eq}}) = 97$ , and  $\gamma(\text{F}_{\text{ax}}\text{ClF}_{\text{ax}}) = 180^\circ$ . The symmetry coordinates were identical to those previously given<sup>23,24</sup> for isoelectronic  $\text{SF}_4$ , except for  $S_3 = \Delta\beta$  and  $S_4 = 0.2765\Delta\alpha_i - 0.8332\gamma$  which are different owing to  $\gamma = 180^\circ$  in  $\text{ClF}_4^+$  and were found numerically by a previously described<sup>40</sup> machine method.

A general valence force field for  $\text{ClF}_4^+$  contains 17 symmetry force constants. Since only nine frequency values are available for their computation, a unique force field cannot be determined. Inspection of the G matrices of  $\text{ClF}_4^+$  shows that in the  $A_1$  block  $G_{12}$ ,  $G_{23}$ , and  $G_{24}$  are zero and, therefore,  $F_{12}$ ,  $F_{23}$ , and  $F_{24}$  can be neglected<sup>41</sup>.

The influence of the remaining off-diagonal F terms on the diagonal F values was determined by computing their values as a function of the off-diagonal F terms. The resulting halves of the force constant ellipses are shown in Figures 11 and 12 and represent the possible mathematical solutions of the force field. It has previously been shown<sup>41</sup> that the most probable range for  $F_{xy}$  is limited by the extremal values  $F_{yy}$  and  $F_{xy} = \text{minimum}$ . Inspection of Figures 11 and 12 reveals that even with this constraint small variation of certain off-diagonal force constants can strongly influence the values of the diagonal force constants. Consequently, an uncertainty of about  $\pm 0.5$   $\text{mdyn}/\text{\AA}$  should be assumed for the stretching force constants  $F_{11}$ ,  $F_{66}$ , and  $F_{88}$ . However, in spite of these relatively larger uncertainties, Figures 11 and 12

clearly show that the symmetry force constants involving the equatorial bonds (i.e.  $F_{11}$  and  $F_{88}$ ) are significantly larger than those involving the axial bonds (i.e.  $F_{22}$  and  $F_{66}$ ). The frequencies used for the force constant computations of  $\text{ClF}_4^+$  are listed in Table III, together with our preferred force field, obtained by assuming plausible interaction terms. The fact that  $\text{ClF}_4^+$  and isoelectronic  $\text{SF}_4$  show similar force fields is not surprising in view of their similar frequencies and G matrices.

The significant difference in covalent bond strength between equatorial (5.1) and axial (3.3 mdyn/ $\text{\AA}$ ) bonds in  $\text{ClF}_4^+$  is in excellent agreement with a generalized bonding scheme previously discussed<sup>42</sup> for a large number of halogen fluorides. It suggests that the bonding in  $\text{ClF}_4^+$  might be explained, as previously described for the related pseudo-trigonal bipyramidal species  $\text{ClF}_3$ ,  $\text{ClF}_3\text{O}$ <sup>40</sup> and  $\text{ClF}_3\text{O}_2$ <sup>39</sup> by the following approximation. The bonding of the three equatorial ligands (including the free electron pair on Cl as a ligand) is mainly due to a  $\text{sp}^2$  hybrid, whereas the bonding of the two axial ClF bonds involves mainly one delocalized p-electron pair of the chlorine atom for the formation of a semi-ionic three-center four-electron  $\text{p}\pi\text{p}\pi$  bond<sup>43-45</sup>.

Bromine Pentafluoride-2 SbF<sub>5</sub> Adduct - The predominantly ionic nature of  $\text{BrF}_5 \cdot 2 \text{SbF}_5$  has previously been established<sup>12</sup> by a single crystal x-ray diffraction study. Owing to the large number of fundamentals expected for  $\text{BrF}_4^+\text{Sb}_2\text{F}_{11}^-$  and to the inavailability of other salts containing the  $\text{BrF}_4^+$  cation only tentative assignments can be made for  $\text{BrF}_4^+$ . These are listed in Table II and are based on comparisons with those reported for iso-electronic  $\text{SeF}_4$ <sup>46-48</sup> and those of other salts containing the  $\text{Sb}_2\text{F}_{11}^-$  anion<sup>20,28,31,33,49</sup>. Our Raman spectrum<sup>1</sup> of solid  $\text{BrF}_4^+\text{Sb}_2\text{F}_{11}^-$  has in the

TABLE III  
 Observed Frequencies ( $\text{cm}^{-1}$ ), Approximate Description of Modes,  
 And Computed Symmetry and Most Important Internal Force Constants<sup>a</sup> of  $\text{ClF}_4^+$

				$\text{ClF}_4^+$	$\text{ClF}_4^+$	$\text{ClF}_3^+$
$A_1$	$\nu_1$	800	$\nu$ sym eq	$F_{11} = \bar{f}_R + f_{RR}$		5.25
				$F_{13} = \sqrt{2} f_{R3}$		0.8
				$F_{14} = f_R$		0.2
$\nu_2$	$\nu_{71}$		$\nu$ sym ax	$F_{22} = f_R + f_{RR}$		3.65
$\nu_3$	$\nu_{10}$		$\delta$ sciss eq	$F_{33} = f_\beta$		2.64
				$F_{34} = f_\alpha$		-0.2
$\nu_4$	237		$\delta$ sciss ax	$F_{44} = 0.31 f_\alpha + 0.69 f_\gamma^C$		0.40
$A_2$	$\nu_5$	475	$\tau$	$F_{55} = f_\alpha + f_\alpha'' - f_\alpha' - f_\alpha'''$		2.08
$B_1$	$\nu_6$	795	$\nu$ as ax	$F_{66} = f_R - f_{RR}$		2.99
				$F_{67} = \sqrt{2} (f_{R\alpha} - f_{R\alpha}')$		0.40
			rocking	$F_{77} = f_\alpha - f_\alpha'' + f_\alpha' - f_\alpha'''$		2.41
$\nu_7$	537		$\nu$ as eq	$F_{88} = f_R - f_{RR}$		4.91
$B_2$	$\nu_8$	829		$F_{89} = \sqrt{2} (f_{R\alpha} - f_{R\alpha}')$		0.6
			$\delta$ sciss ax out of plane	$F_{99} = f_\alpha - f_\alpha'' - f_\alpha' + f_\alpha'''$		2.45
				$f_R$		5.08
				$f_R$		3.32
				$f_{RR}$		0.17
				$f_{RR}$		0.35
						0.36

(a) Stretching constants in  $\text{mdyn}/\text{\AA}$ , deformation constants in  $\text{\AA}/\text{radian}^2$ , and stretch-bend interaction constants in  $\text{mdyn}/\text{radian}$ .

(b) Ref. 25

(c) In addition to interaction constants which are not listed.

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meantime been confirmed by Surles et al.<sup>13</sup> and the proposed assignments<sup>1,13</sup> agree for most of the fundamentals. Since the crystal structure of  $\text{BrF}_4^+\text{Sb}_2\text{F}_{11}^-$  is known<sup>12</sup> and the assignments for  $\text{BrF}_4^+$  are tentative, no force constant computations were carried out for  $\text{BrF}_4^+$ .

Iodine Pentafluoride-SbF<sub>5</sub> Adduct - Two independent single crystal x-ray diffraction studies<sup>16,17</sup> have shown that the  $\text{IF}\cdot\text{SbF}_5$  has the predominantly ionic structure  $\text{IF}_4^+\text{SbF}_6^-$ , although the bond lengths and angles found by the two groups for  $\text{IF}_4^+$  differ somewhat. The observed vibrational spectrum of  $\text{IF}_5\cdot\text{SbF}_5$  (see Table II) is consistent with such a predominantly ionic structure. The bands were tentatively assigned by comparison with those of  $\text{TeF}_4^{48}$ , which is isoelectronic with  $\text{IF}_4^+$ , and those reported for similar  $\text{SbF}_6^-$  salts<sup>20,30</sup> containing an  $\text{SbF}_6^-$  anion distorted from symmetry  $\text{O}_h^{50}$ . Our Raman spectrum of  $\text{IF}_5\cdot\text{SbF}_5$  is in good agreement with that reported<sup>18</sup> by Shamir and Yaroslavski. However, their interpretation suffers from the incorrect assumption of an ideal octahedral  $\text{SbF}_6^-$  anion. As for  $\text{BrF}_4^+\text{Sb}_2\text{F}_{11}^-$ , the tentative nature of the  $\text{IF}_4^+$  assignments does not warrant a force constant treatment.

In summary, all the experimental data, i.e., x-ray diffraction data, vibrational and <sup>19</sup>F nmr spectra, and conductivity measurements, available for the halogen pentafluoride-Lewis acid adducts are consistent with predominantly ionic structures containing  $\text{Hal F}_4^+$  cations. The structure of these cations can be derived from a pseudo-trigonal bipyramide with a free valence electron pair occupying one of the equatorial positions. Deviation from this structure increases, as expected, with increasing size and polarizability of the halogen central atom. This results in a decrease of

the axial F-Hal-F angle and increasing F bridging from the  $\text{ClF}_5$  to the  $\text{IF}_5$  adducts. A comparison of the fundamentals assigned to the  $\text{Hal F}_4^+$  cations with those of the isoelectronic chalcogen tetrafluoride series (see Table IV) shows consistent trends and satisfactory agreement.

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TABLE IV  
 Comparison of the Fundamental Vibrations of  $\text{ClF}_4^+$ ,  $\text{BrF}_4^+$ , and  $\text{IF}_4^+$   
 With Those of Isoelectronic  $\text{SF}_4$ ,  $\text{SeF}_4$ , and  $\text{TeF}_4$ , Respectively

		$\text{ClF}_4^+$	$\text{BrF}_4^+$	$\text{IF}_4^+$	$\text{SF}_4$	$\text{SeF}_4$	$\text{TeF}_4$
$A_1$	$v_1$	800	723	704	891	749	695
	$v_2$	571	606	609	553	574	572
	$v_3$	510	385	341	475	366	293
	$v_4$	237	216	151	226	162	[151] <sup>a</sup>
$A_2$	$v_5$	475	--	--	414	--	--
$B_1$	$v_6$	795	704	655	730	622	587
	$v_7$	537	419	385	532	400	333
$B_2$	$v_8$	829	736	720	867	723	682
	$v_9$	385	369	316	353	250	[184.8] <sup>a</sup>

(a) Computed values

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Diagram Captions

Figure 1 - Raman spectrum of solid  $\text{ClF}_5 \cdot 1.08 \text{ SbF}_5$  (Sample I) contained in Teflon FEP capillary. Exciting line was 5145 Å. C indicates spectral slit width.

Figure 2 - Raman spectrum of solid  $\text{ClF}_5 \cdot 1.36 \text{ SbF}_5$ . Traces A and B show Samples II and III, respectively. Kel-F capillaries were used as containers with 5145 Å excitation.

Figure 3 - Infrared spectra of solid  $\text{ClF}_5 \cdot x \text{SbF}_5$  as dry powder between AgBr plates. Trace A, Sample II; trace B, Sample I; trace C, AgBr window background.

Figure 4 - Raman spectrum of solid  $\text{ClF}_5 \cdot \text{AsF}_5$  contained in Teflon FEP capillary. Exciting was line 5145 Å. Bands marked by an asterisk are due to the Teflon tube.

Figure 5 - Low-temperature infrared spectrum of solid  $\text{ClF}_5 \cdot \text{AsF}_5$ . Window material AgCl.

Figure 6 - Raman spectrum of solid  $\text{BrF}_5 \cdot 2 \text{ SbF}_5$  contained in glass tube with hollow inside glass cone. Exciting was line 5145 Å using the axial viewing-transverse excitation technique.

Figure 7 - Infrared spectrum of solid  $\text{BrF}_5 \cdot 2 \text{ SbF}_5$  as dry powder between AgCl plates.

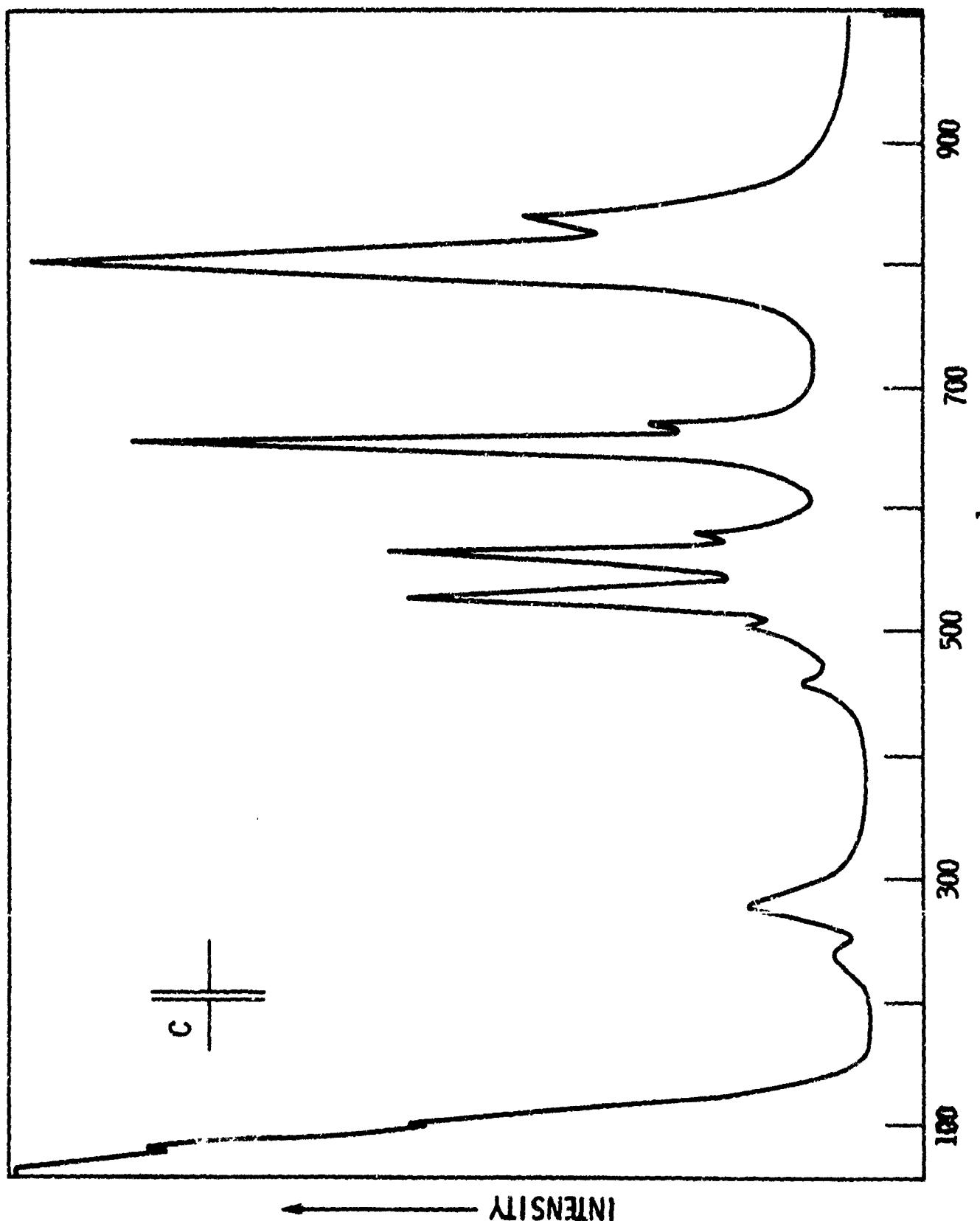
Figure 8 - Raman spectrum of solid  $\text{IF}_5 \cdot \text{SbF}_5$  contained in glass tube with hollow inside glass cone using  $5145 \text{ \AA}$  excitation.

Figure 9 - Infrared spectrum of solid  $\text{IF}_5 \cdot \text{SbF}_5$  as dry powder between AgBr plates.

Figure 10 - Raman spectra of HF solutions of  $\text{IF}_5 \cdot \text{SbF}_5$  (trace A),  $\text{BrF}_5 \cdot 2 \text{ SbF}_5$  (trace B),  $\text{ClF}_5 \cdot 1.00 \text{ SbF}_5$  (trace C),  $\text{ClF}_2^+ \text{SbF}_6^-$  (trace D, the numbers indicate  $v_1$ ,  $v_2$ , and  $v_5$  of octahedral  $\text{SbF}_6^-$ ) in Teflon-FEP capillaries using  $4880 \text{ \AA}$  excitation. Trace E shows the spectrum of an empty capillary; Teflon bands are marked by an asterisk. F indicates spectral slit width.

Figure 11 - Force Constant Ellipses for  $\text{ClF}_4^+$ . The solid and broken curves represent the solutions for  $F_{11}$ ,  $F_{33}$ , and  $F_{44}$  as a function of  $F_{34}$  and for  $F_{11}$  and  $F_{33}$  as a function of  $F_{13}$ , respectively. Dimensions are in  $\text{mdyn}/\text{\AA}^0$ .

Figure 12 - Force Constant Ellipses for  $\text{ClF}_4^+$ . The solid, broken, and dotted curves represent the solutions for  $F_{11}$ ,  $F_{33}$ , and  $F_{44}$  as a function of  $F_{14}$ , for  $F_{66}$  and  $F_{77}$  as a function of  $F_{67}$ , and for  $F_{88}$  and  $F_{99}$  as a function of  $F_{89}$ , respectively.

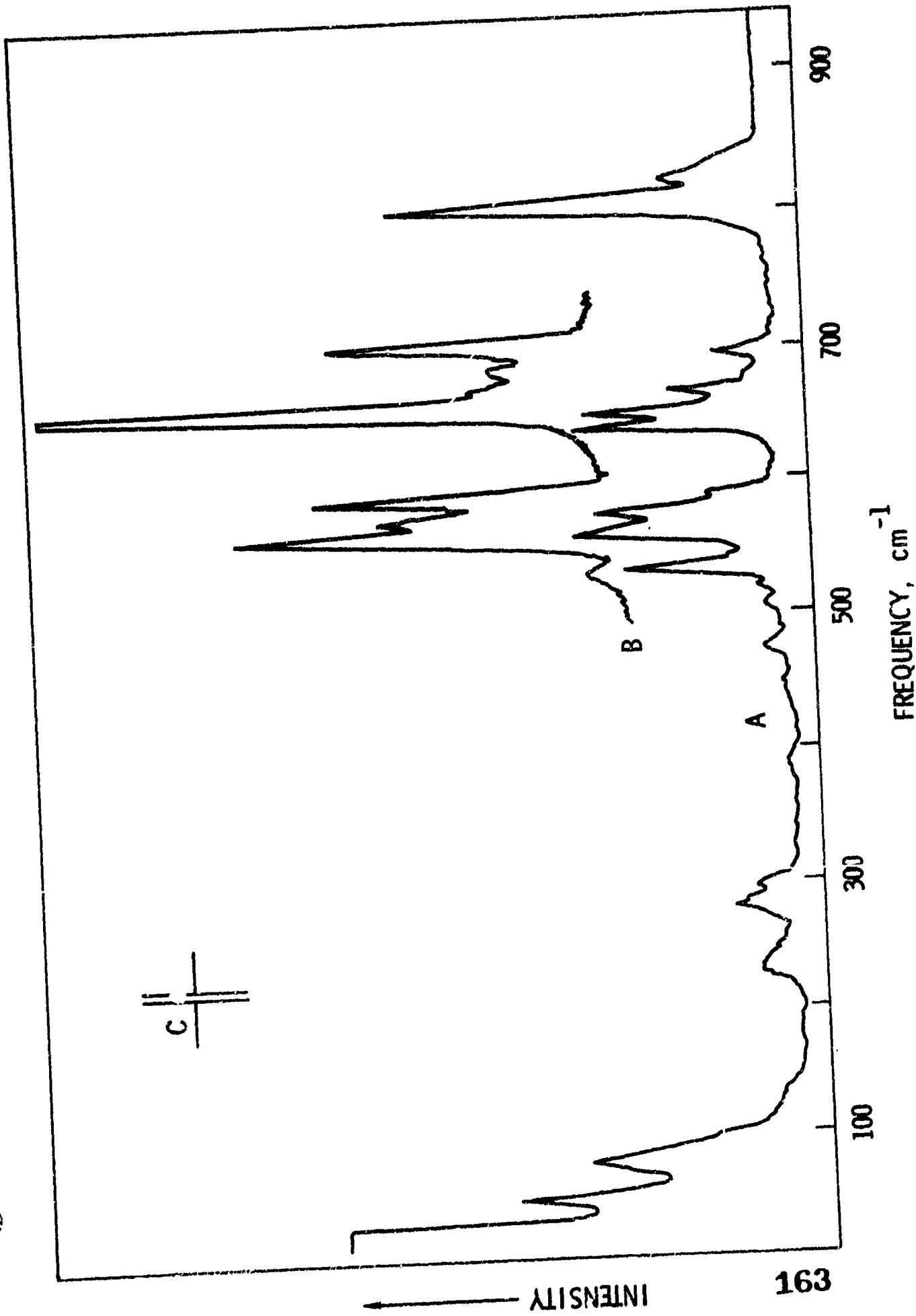


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Figure 1



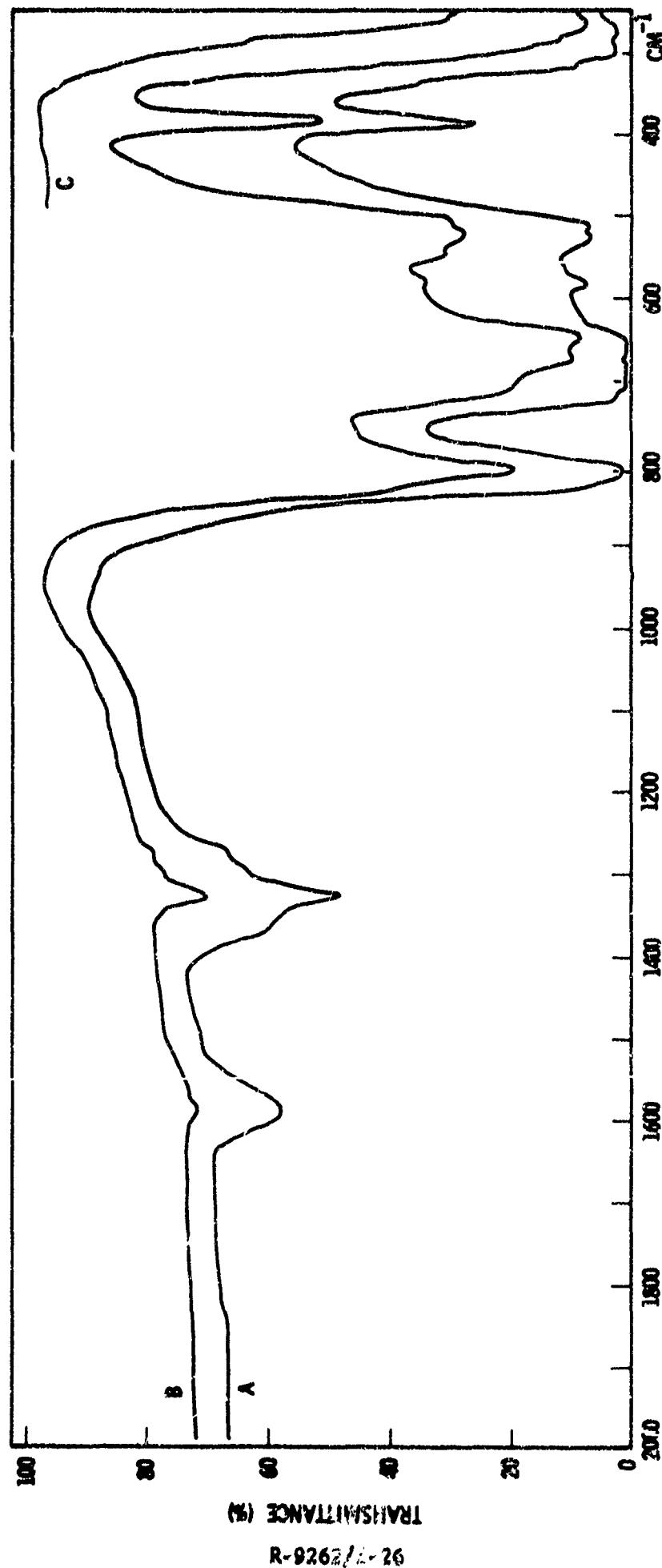


Figure 3

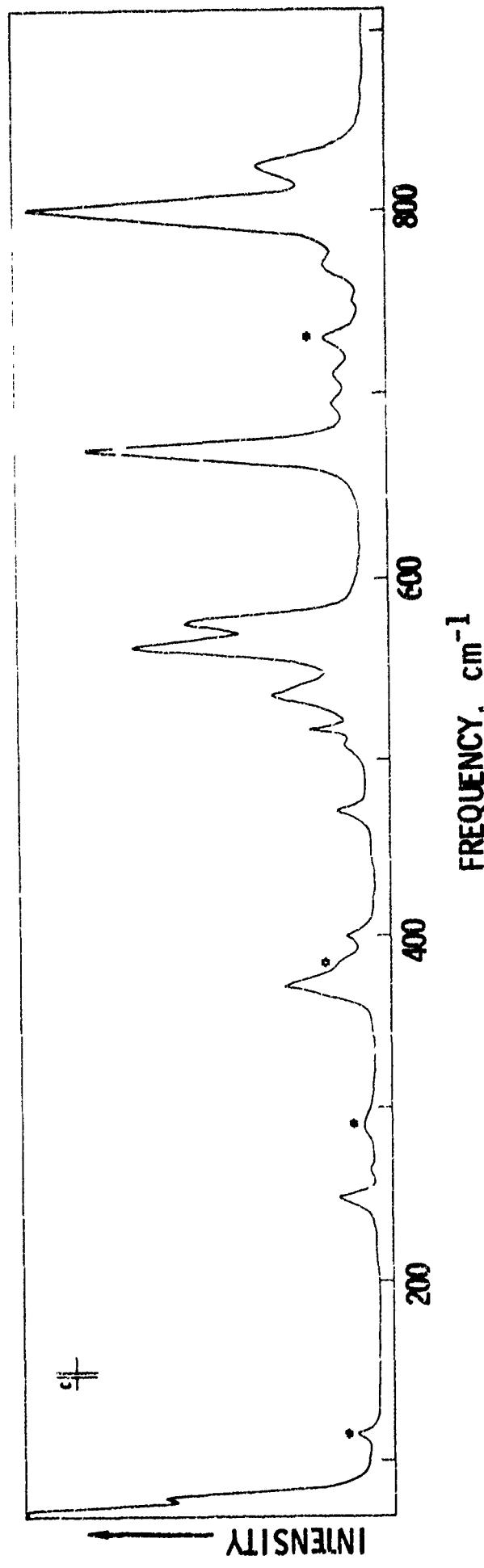


Figure 4

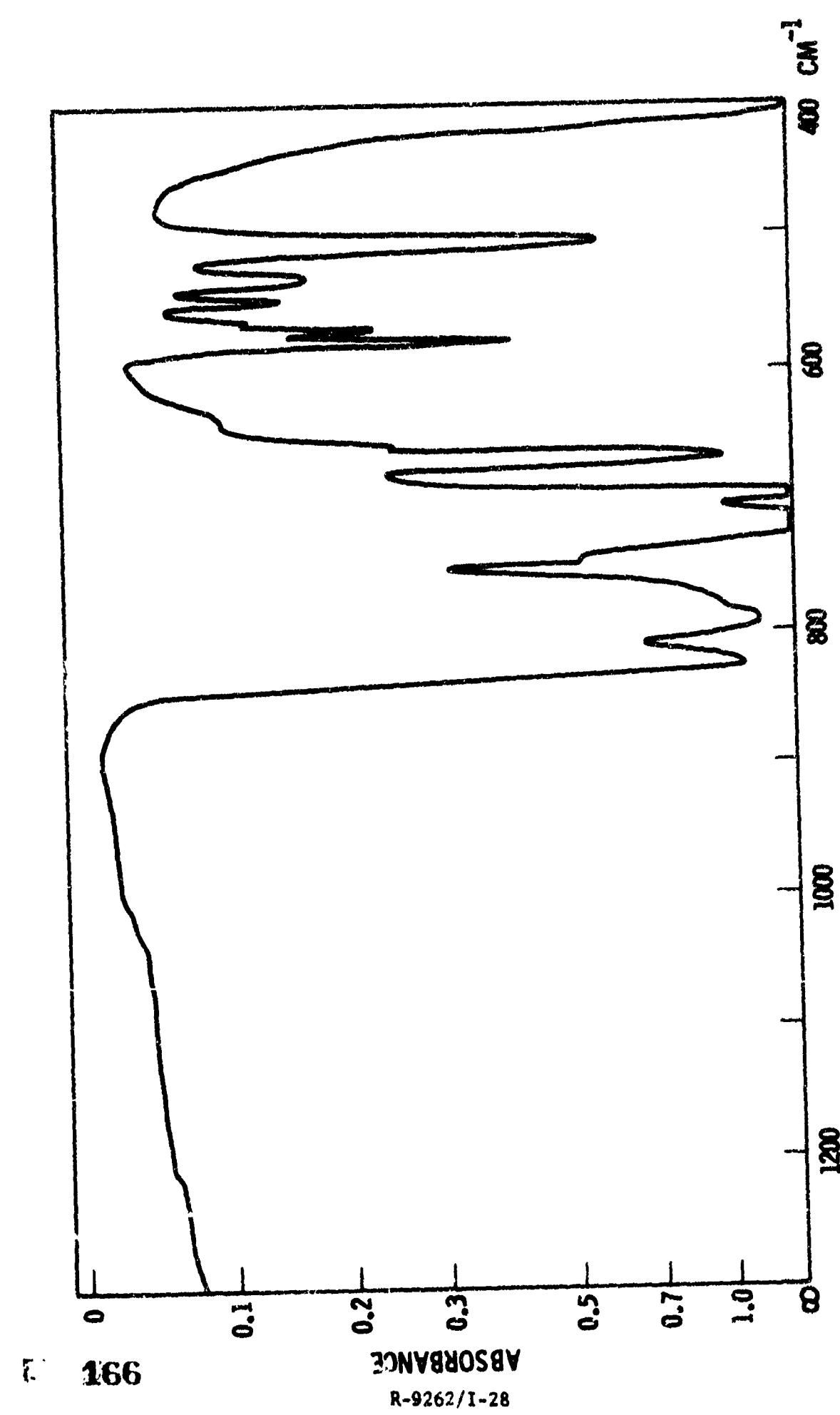
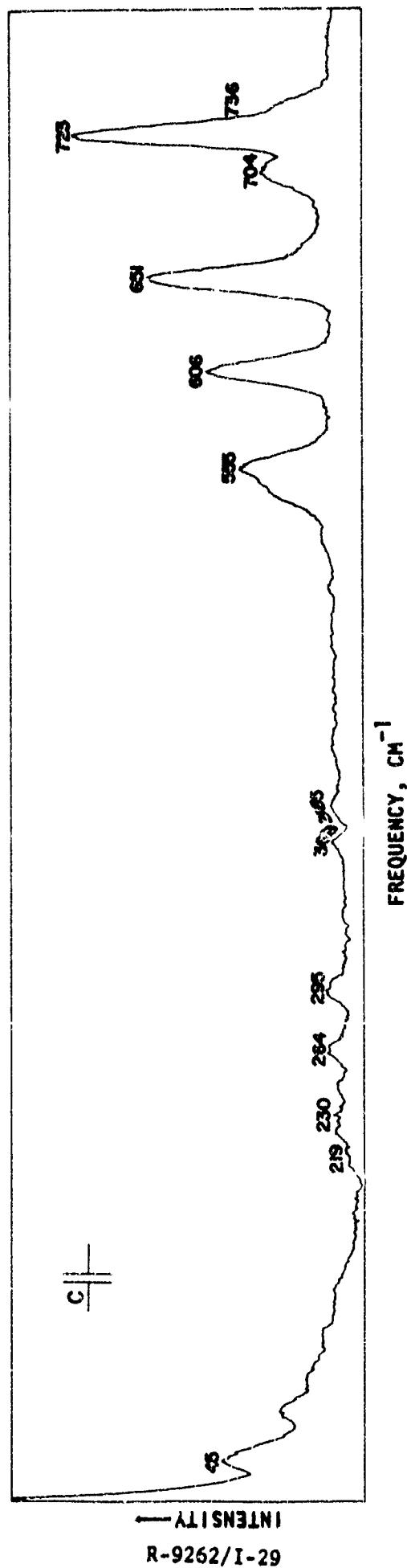


Figure 5



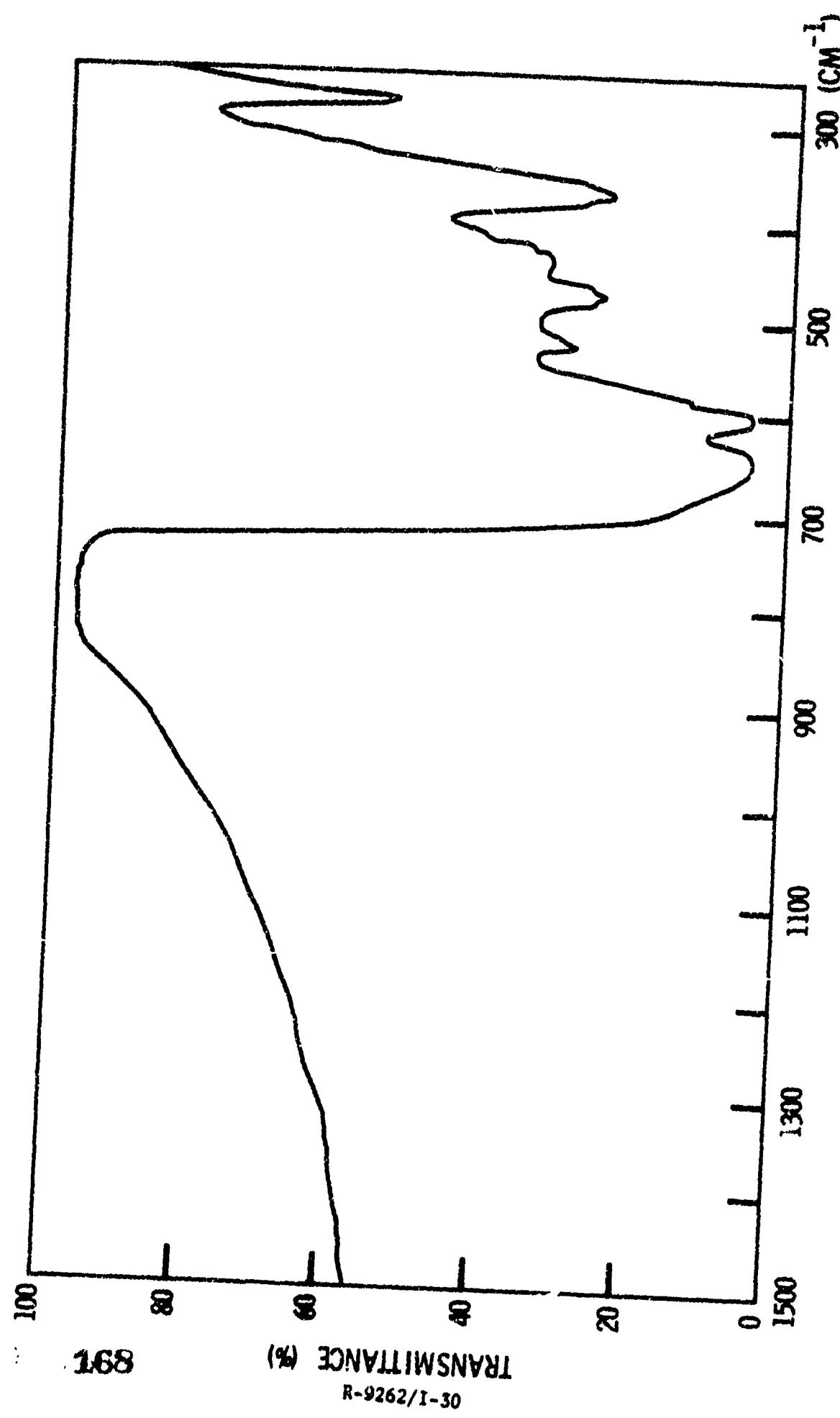
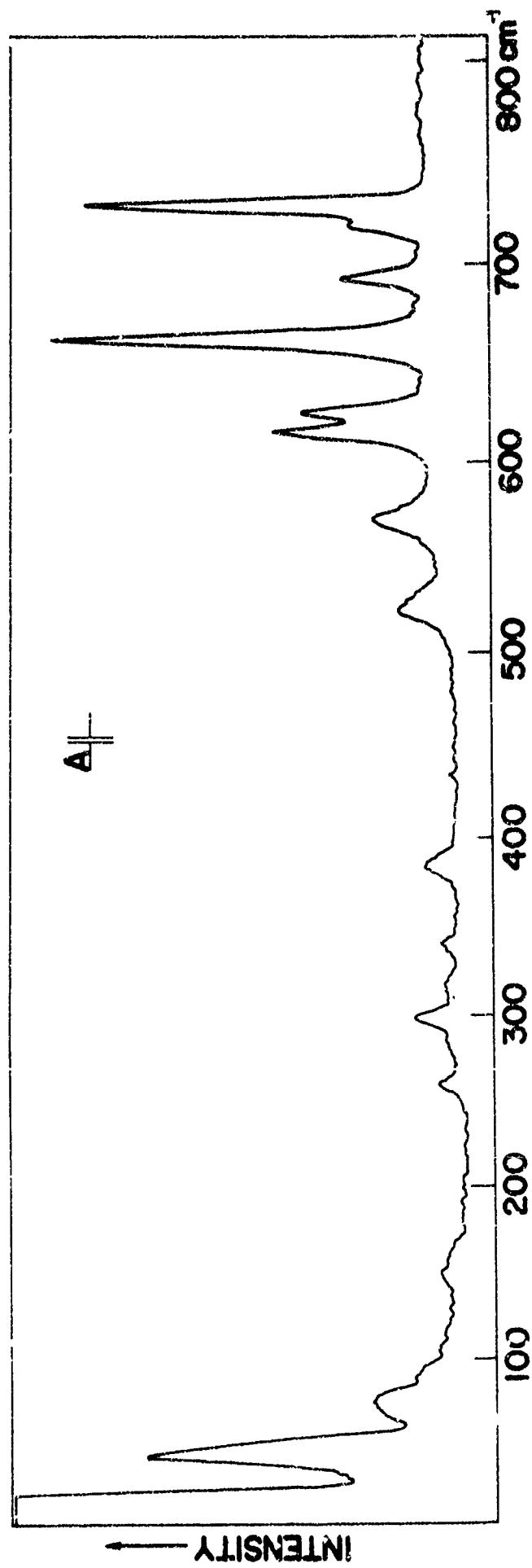


Figure 7



R-9262/I-31

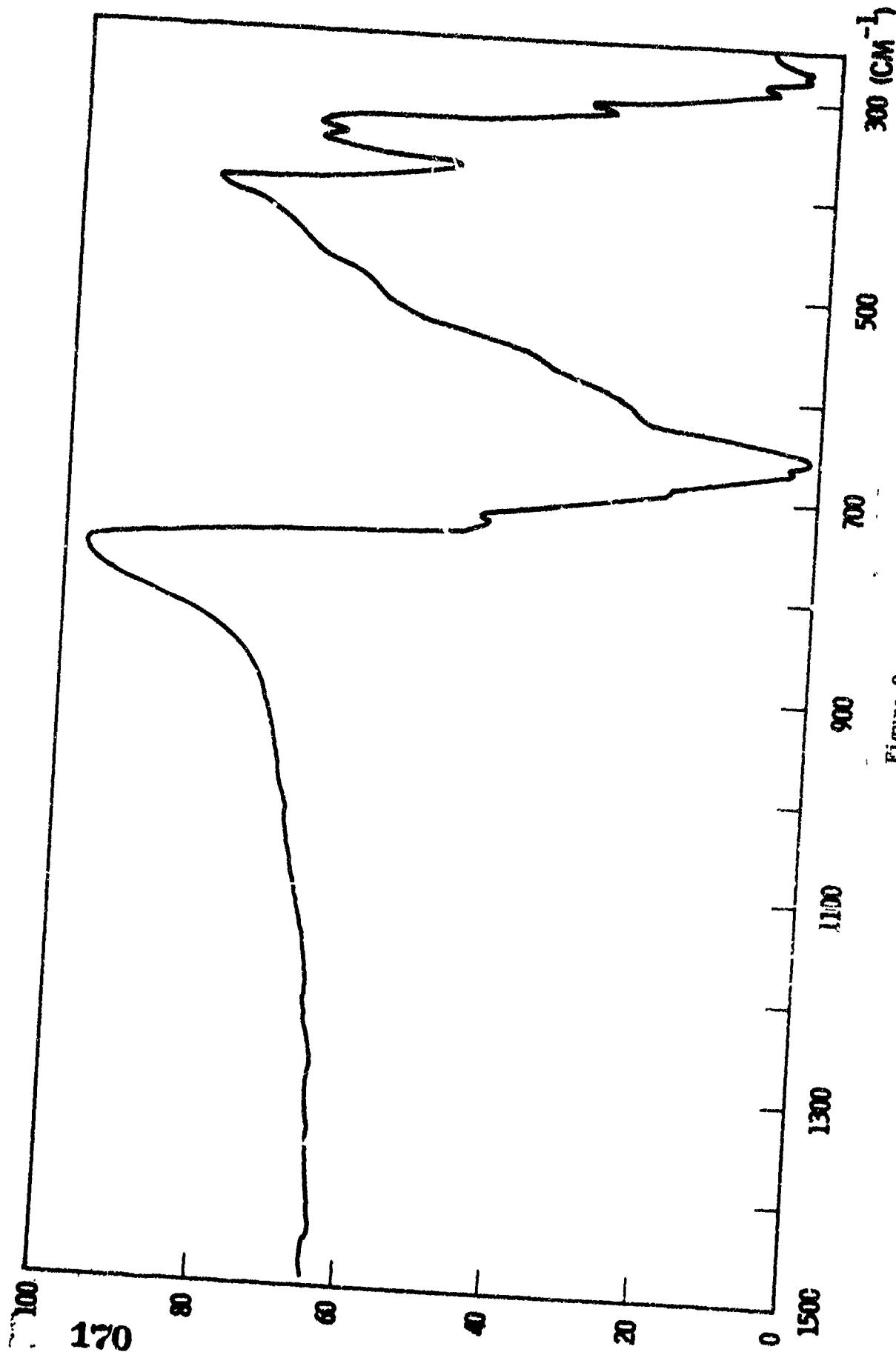


Figure 9

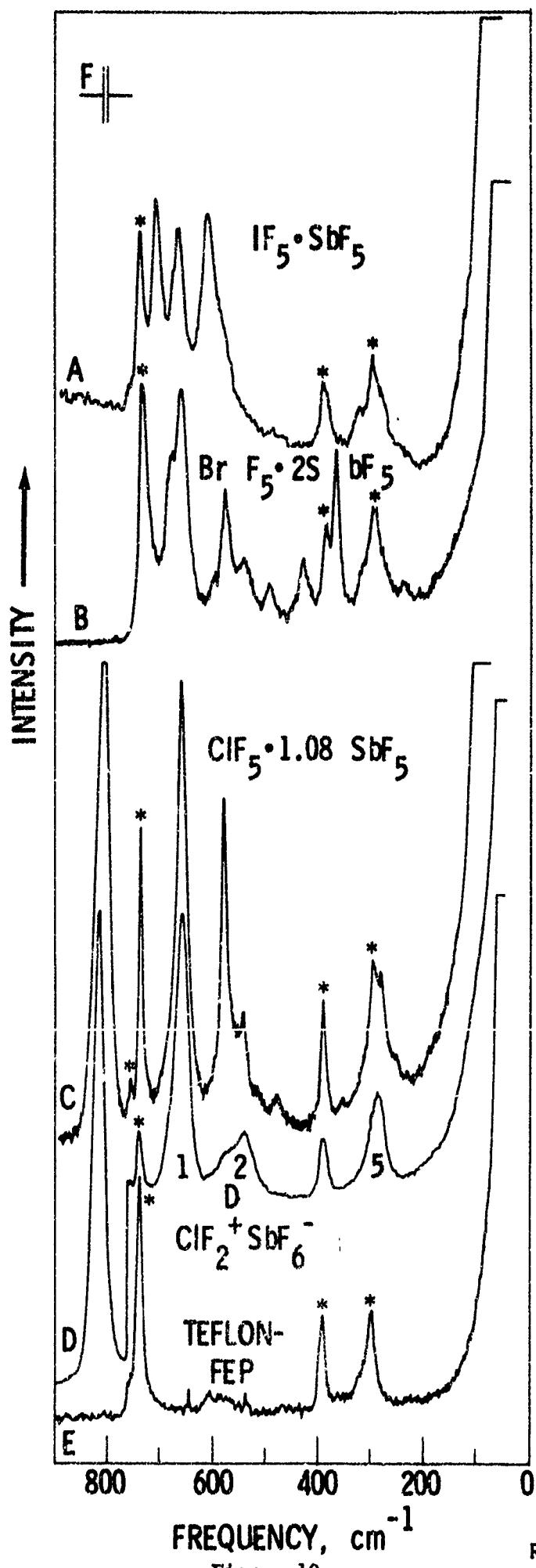
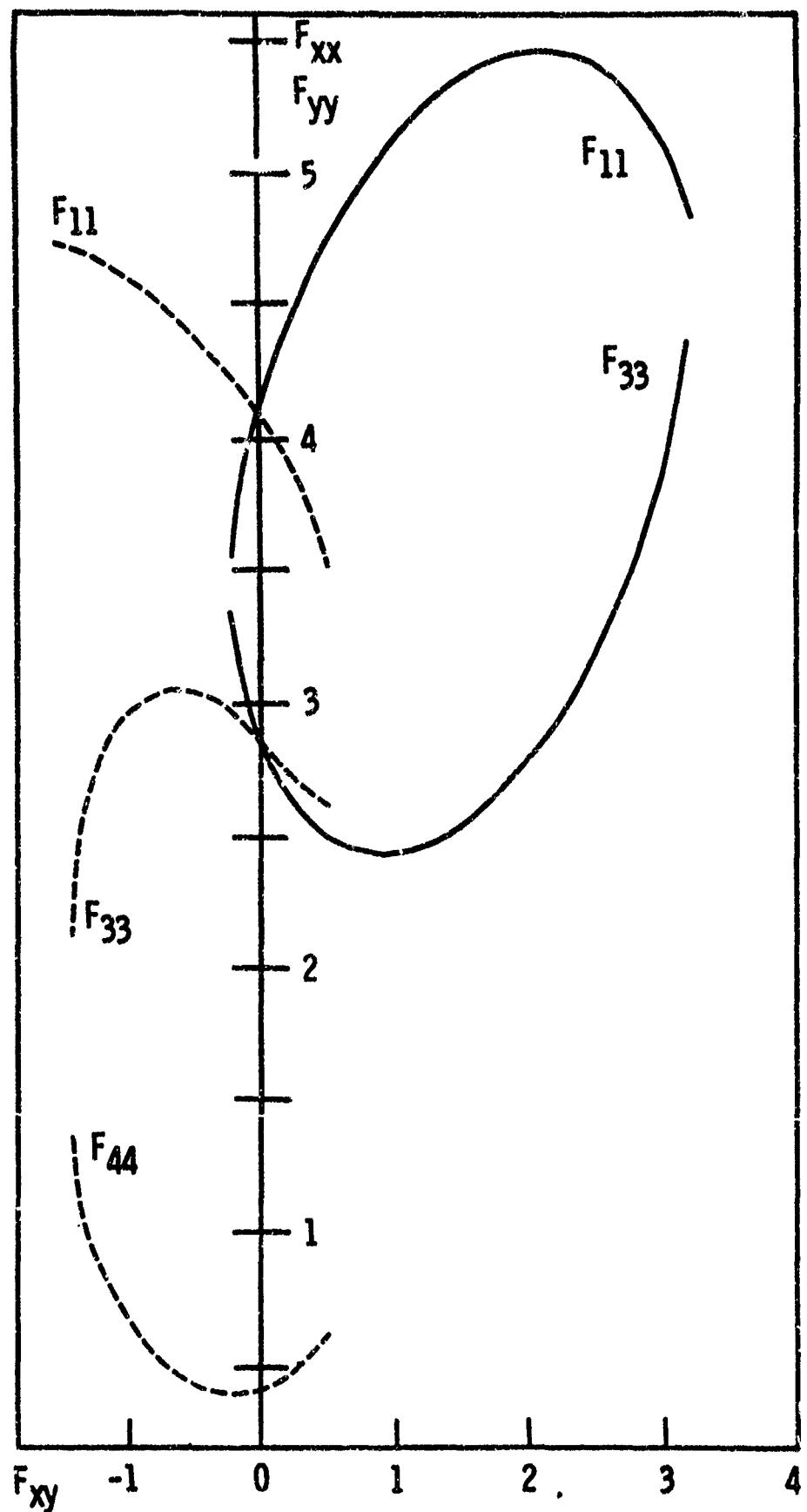


Figure 10

R-9262/I-33



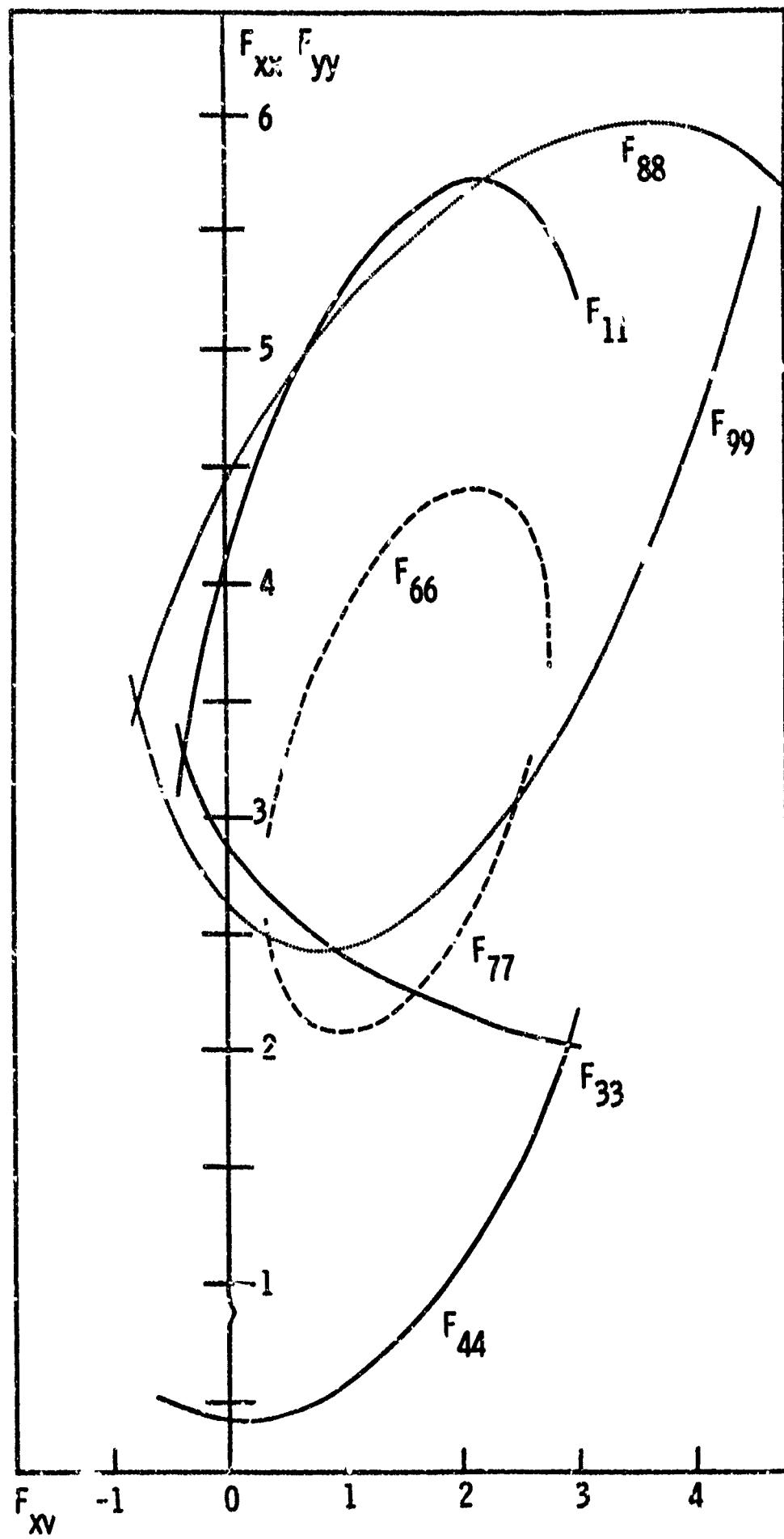


Figure 12

R-9262/I-35/I-36

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## VIBRATIONAL ASSIGNMENT OF SF<sub>4</sub>

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In a previous paper<sup>1</sup> we reported the Raman spectrum of gaseous SF<sub>4</sub>. The Raman data and a reinterpretation of the infrared band contours suggested the need of revising all assignments for the deformational modes except for v<sub>7</sub> (B<sub>1</sub>). For the four stretching modes, the previous assignment<sup>2-4</sup> was adopted and force constants and mean amplitudes of vibration were computed.<sup>1</sup> In a recent paper,<sup>5</sup> Frey, Redington, and Aljibury proposed a reversed assignment for the two antisymmetric stretching modes, v<sub>6</sub> (B<sub>1</sub>) and v<sub>8</sub> (B<sub>2</sub>), based on a comparison with the spectra of the structurally related molecules, BrF<sub>3</sub> and ClF<sub>3</sub>. More recently, Levin<sup>6</sup> proposed a reassignment of the deformational modes on the basis of Raman and infrared spectra of solid SF<sub>4</sub> and supported his assignment with a CNDO/2 calculation of the infrared intensities. One of Levin's main arguments for revising the assignment of the deformational modes was the observation of two bands at 245 and 205 cm<sup>-1</sup>, respectively, in the Raman spectrum of solid SF<sub>4</sub>. In a subsequent paper,<sup>7</sup> however, Berney showed that the 205 cm<sup>-1</sup> Raman band is due to residual  $\alpha$ -SF<sub>4</sub>.

Another unsettled question involves the frequencies of the axial and equatorial SF<sub>2</sub> scissoring modes in species A<sub>1</sub>. It was shown<sup>8-12</sup> for related trigonal bipyramidal molecules such as PF<sub>5</sub> that these two deformational modes are highly mixed,<sup>11</sup> and that a better agreement with the observed mean square amplitudes of vibration can be achieved<sup>10</sup> by assigning the lower frequency to

the equatorial deformation. This frequency sequence was also proposed by Levin<sup>6</sup> for SF<sub>4</sub>, contrary to our assignment<sup>1</sup> and that of Frey et al.<sup>5</sup> which are more consistent with the fact that in SF<sub>4</sub> the equatorial bonds are considerably shorter and hence stronger than the equatorial ones.<sup>13,14</sup> In view of these conflicting assignments, we have recomputed the force field and mean square amplitudes of vibration for SF<sub>4</sub> hoping that these data might allow us to distinguish between the different assignments<sup>1,5,6</sup> (see Table 1).

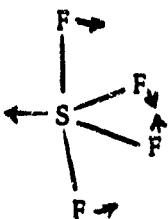
Since only nine frequency values are available for the computation of seventeen symmetry force constants, a General Valence Force Field cannot be computed. However, it is known that mean square amplitudes of vibration are only slightly influenced by moderate changes in the force field. This was confirmed for SF<sub>4</sub> by calculating mean amplitudes of vibration based on two force fields obtained by two different approximating methods. The first method used was the eigenvector method,<sup>15,16</sup> and the second one was a diagonal MVFF for species A<sub>1</sub> and B<sub>2</sub> combined with the F<sub>67</sub> = minimum solution for species E<sub>1</sub> since no real values can be obtained for F<sub>67</sub> = 0. The results of these computations are given in Tables 2, 3, and 4, and in Figure 1. The mean square amplitudes of vibration computed from the two force fields differed by less than 0.001 Å, except for <q<sup>2</sup>>1/2 F<sub>3...F<sub>4</sub></sub> using the assignment of Levin<sup>6</sup> which showed a difference of 0.004 Å. Therefore, only the data obtained by the eigenvector method are listed in Tables 2, 3, and 4, except for the preferred (see below) set II, for which the MVFF values are also given for comparison.

Table 1 and Figure 1 show that the mean square amplitudes of vibration are useful for discriminating between the different assignments of the deformational modes, but are of little help in finding the correct assignment for the two stretching modes v<sub>6</sub>(B<sub>1</sub>) and v<sub>8</sub>(B<sub>2</sub>). However, the following force field arguments favor set II over set I: (1) Generally, the stretch-stretch interaction constant is relatively small whenever two bonds form an angle close to 90°. In set I, the equatorial interaction constant f<sub>r'</sub> exhibits a value of 1.21 mdyn/Å which is unreasonably high for a F-S-F bond angle of 101°. The value of 0.49 mdyn/Å obtained for set II is much more plausible; (2) The value of the second stretch-stretch interaction constant, f<sub>R'</sub>, shows

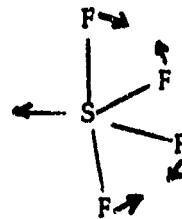
only for set II a value similar to those observed for the related species,  $SF_5^{-17}$ ,  $ClF_3^5$ , and  $BrF_3^5$ ; (3) The bond length of the equatorial S-F bonds in  $SF_4$  ( $1.545 \pm 0.003 \text{ \AA}$ )<sup>14</sup> is similar to that in  $SF_6$  ( $1.56 \pm 0.02 \text{ \AA}$ )<sup>18</sup>. Since bond lengths are related to the stretching force constants, one might expect  $f_r$  of  $SF_4$  to approach the  $SF_6$  value<sup>19</sup> of 5.26 mdyne/ $\text{\AA}$ . This is true only for set II; (4) The relatively large difference in the length of the equatorial and the axial bonds of  $SF_4$  ( $0.10 \text{ \AA}$ )<sup>14</sup> favors set II which shows the larger difference between  $f_r$  and  $f_R$ ; (5) Set II is in better agreement with the values found<sup>17</sup> for  $SF_5^-$  if the general decrease in the force constant values owing to the formal negative charge is taken into account. Thus, the proposed<sup>5</sup> reassignment of  $\nu_6(B_1)$  and  $\nu_8(B_2)$  results in a more satisfactory set of force constants for  $SF_4$ , although it remains difficult to rationalize the observed infrared band contours.<sup>2,4</sup>

The question as to which  $A_1$  deformation mode should be assigned to the higher frequency value, can readily be decided based on the computed mean square amplitudes of vibration (see Table 4 and Figure 1). It should be noted that the  $F_1 \dots F_3$  values reported in our previous paper<sup>1</sup> are incorrect due to a computational error. The revised values are listed as set Ia. It can be seen from Figure 1 that all b set: (i.e.  $\delta$  sciss ax >  $\delta$  sciss eq) result in unacceptably high values for  $\langle q \rangle^{1/2} F_3 \dots F_4$ . Hence,  $\delta$  sciss eq >  $\delta$  sciss ax appears to be a better description of the two  $A_1$  deformational modes of  $SF_4$ . It should be kept in mind, however, that both  $\nu_3$  and  $\nu_1$  are not highly characteristic. The potential energy distribution obtained for the diagonal force field shows that  $\nu_3$  is made up of 65% equatorial and 35% axial bending motion, and that  $\nu_1$  contains significant contributions from both the axial and equatorial bending motions. This high degree of mixing is not surprising since the G matrix elements  $G_{13}$ ,  $G_{14}$ , and  $G_{34}$  of  $SF_4$  show large numerical values. The two remaining modes in species  $A_1$  are more characteristic:  $\nu_2$  is made up entirely of axial stretching and  $\nu_4$  represents 88% axial bending. As can be seen from Figure 1, the fit between observed<sup>13</sup> and computed  $\langle q \rangle^{1/2} F_3 \dots F_4$  and  $F_1 \dots F_3$  can be improved by increasing somewhat the mixing between  $\nu_3$  and  $\nu_4$ . However, this increase is too small to justify reversing the assignment of  $\nu_3$  and  $\nu_4$ . Additional support for  $\nu_3 > \nu_4$  in the chalcogen tetrafluorides was recently obtained<sup>21</sup> by Adams and Downs in a matrix isolation study of  $SeF_4$ . The observed selenium isotopic shifts show that the higher frequency value belongs to  $\nu_3$ .

The high degree of mixing between the equatorial and axial bending motions for  $v_3$  can be rationalized. Inspection of the normal coordinates of  $v_3$  shows that this mode is essentially an umbrella type deformation, i.e. a symmetric combination of the equatorial and axial bending motions. The  $v_4$  deformation might be considered as the corresponding anti-symmetric combination of these motions. It should be the mode mainly involved in an intramolecular exchange process as suggested by Berry,<sup>22</sup> although higher vibrational levels must be invoked since the normal coordinates show only little motion of the equatorial fluorines in the fundamental. The fact that the PED shows  $v_4$  to be composed mainly of axial bending is due



$v_3$ , symmetric combination  
of axial and equatorial bending



$v_4$ , antisymmetric combination  
of axial and equatorial bending

to the fact that the sulfur moves in the same direction as the equatorial fluorines thus suppressing the equatorial scissoring motion.

Inspection of Figure 1 also reveals that the assignment proposed<sup>6</sup> by Levin (set IIIb) results in unsatisfactory values for  $\langle q^2 \rangle^{1/2} F_3 \dots F_4$  and  $F_1 \dots F_3$  and, therefore, should be rejected. Furthermore, it can be seen that retaining Levin's frequencies<sup>6</sup> for  $A_1$  but reversing the assignment of  $v_3$  and  $v_4$  (set IIIa) results in too high a value for  $\langle q^2 \rangle^{1/2} F_1 \dots F_3$ . This discrepancy cannot be eliminated by increasing the mixing between  $v_3$  and  $v_4$ , since a small decrease in  $\langle q^2 \rangle^{1/2} F_1 \dots F_3$  results in a large increase in  $\langle q^2 \rangle^{1/2} F_3 \dots F_4$ . A second strong argument against set IIIa was recently put forward<sup>7</sup> by Berney. He showed that the splitting of the  $223 \text{ cm}^{-1}$  Raman line in the spectrum of the solid is due to the  $\alpha$ ,  $\beta$ , and  $\gamma$  forms of  $\text{SF}_4$  and not due to two different fundamentals, thus eliminating the basis of Levin's reassignment. Furthermore, the observed infrared band contours<sup>4</sup> and Raman polarization measurements on gaseous  $\text{SF}_4$ <sup>1</sup> and  $\text{SeF}_4$ <sup>23</sup> favor set II over III.

Since the MVFF obtained by the eigenvector method<sup>15,16</sup> is not too different from the diagonal force field, numerical experiments were carried out by varying the off diagonal constants within meaningful limits. Whereas for set IIa, the fit between observed and computed  $\langle q^2 \rangle^{1/2} F_1 \dots F_3$  could be improved, for set IIb the large discrepancy in  $\langle q^2 \rangle^{1/2} F_3 \dots F_4$  could not be eliminated.

In summary, set IIa is the only assignment which can satisfy both the observed<sup>13</sup> mean square amplitudes of vibration and basic force field arguments. Furthermore, the mean square amplitudes of vibration suggest that for SF<sub>4</sub> the higher frequency A<sub>1</sub> deformational mode v<sub>3</sub> should be assigned to the equatorial scissoring motion. However, a normal coordinate description of v<sub>3</sub> and v<sub>4</sub> as symmetric and antisymmetric combinations, respectively, of the equatorial and axial scissoring motions seems more appropriate.

#### ACKNOWLEDGMENT

We thank Drs. E. C. Curtis, D. Pilipovich and C. J. Schack, Rocketdyne, for many helpful discussions. This work was in part supported by the U. S. Office of Naval Research, Power Branch.

Table 1  
Assignment of Normal Modes of  $SF_4$

Species	Approximate Description	Assignment		
		I Christe and Sawodny <sup>a</sup>	II Frey et al. <sup>b</sup>	III Levin <sup>c</sup>
$A_1$ $\nu_1$	$\nu$ sym $SF_2$ eq	892	892	892
$\nu_2$	$\nu$ sym $SF_2$ ax	558	558	558
$\nu_3$	$\delta$ sciss $SF_2$ eq	475	475	245 (233)
$\nu_4$	$\delta$ sciss $SF_2$ ax in plane	226	228	353
$A_2$ $\nu_5$	$SF_2$ twist	414	414	475
$B_1$ $\nu_6$	$\nu$ asym $SF_2$ ax	867	730	728
$\nu_7$	$SF_2$ rocking	532	532	533
$B_2$ $\nu_8$	$\nu$ asym $SF_2$ eq	730	867	867
$\nu_9$	$\delta$ sciss $SF_2$ ax out of plane	353	353	206 (228)

a ref. 1

b ref. 5

c ref. 6

Table 2

Symmetry Force Constants <sup>a,b</sup> of SF<sub>4</sub> Computed from the Assignments Listed in Table 1 Assuming for Sets a  
 $\delta SF_2 \text{ eq } > \delta SF_2 \text{ ax}(A_1)$  and for Sets b  $\delta SF_2 \text{ eq } < \delta SF_2 \text{ ax } (A_1)$

		Ia	Ib	IIa	IIa(MVFF)	IIb	IIIa	IIIb
$A_1$	$F_{11}$	5.74	5.71	5.74	5.49	5.71	5.83	5.81
	$F_{22}$	3.48	3.48	3.48	3.48	3.48	3.48	3.48
	$F_{33}$	1.97	0.57	1.97	2.10	0.57	1.10	0.63
	$F_{44}$	0.37	1.30	0.37	0.38	1.30	0.41	0.71
	$F_{12}$	0	0.01	0	0	0.01	0	0
	$F_{13}$	0.13	0.05	0.13	0	0.05	0.02	0.04
	$F_{14}$	0.05	0.16	0.05	0	0.16	0.04	0.05
	$F_{23}$	0.02	0.01	0.02	0	0.01	0	0
	$F_{24}$	0.01	0.02	0.01	0	0.02	0.01	0.01
	$F_{34}$	-0.04	-0.03	-0.04	0	-0.03	-0.07	-0.06
$A_2$	$F_{55}$ ( $\nu_5 = 200 \text{ cm}^{-1}$ )			0.35				
	( $\nu_5 = 400 \text{ cm}^{-1}$ )			1.40				
	( $\nu_5 = 600 \text{ cm}^{-1}$ )			3.15				
$B_1$	$F_{66}$	3.66	3.66	2.65	2.35	2.65	2.65	2.65
	$F_{77}$	2.20	2.20	2.24	2.50	2.24	2.24	2.24
	$F_{67}$	0.45	0.45	0.60	0.54 <sup>c</sup>	0.60	0.60	0.60
$B_2$	$F_{88}$	3.33	3.33	4.77	4.62	4.77	4.77	4.77
	$F_{99}$	2.01	2.01	1.98	2.04	1.98	1.98	1.98
	$F_{89}$	0.20	0.20	0.17	0	0.17	0.17	0.17

a) Stretching force constants in mdyn/Å, deformation constants in mdyn Å, and stretch-bend interaction constants in mdyn.

b) Unless otherwise indicated the listed force fields were computed by the eigenvector method.

c) Minimum value of  $F_{67}$  required for obtaining a real solution.

Table 3

Stretching Force Constants (in mdyn/Å) and Bond Lengths (in Å)  
of  $\text{SF}_4$  Compared to Those of Related Molecules and Ions

	Ia	$\text{SF}_4$	IIa	IIa(MVFF)	IIIb	$\text{SF}_6^a$	$\text{SF}_5^b$	$\text{ClF}_3^c$
$f_R$ (ax)	3.57	3.07	2.92	2.92	3.07		2.06	2.70
$f_R'$	-0.09	0.42	0.57	0.57	0.42		0.52	0.36
$f_r$ (eq)	4.54	5.25	5.05	5.05	5.33	5.26	4.12	4.19
$f_r'$	1.21	0.49	0.43	0.43	0.48			
R			1.646 $\pm$ 0.003 <sup>d</sup>					
r			1.545 $\pm$ 0.003 <sup>d</sup>		1.56 $\pm$ 0.02 <sup>e</sup>			

a ref. 19

b ref. 17

c ref. 5

d ref. 14

e ref. 18

Table 4

Computed and Observed  $^{13}$  Mean Square Amplitudes  
(in Å) of Vibration of  $\text{SF}_4$

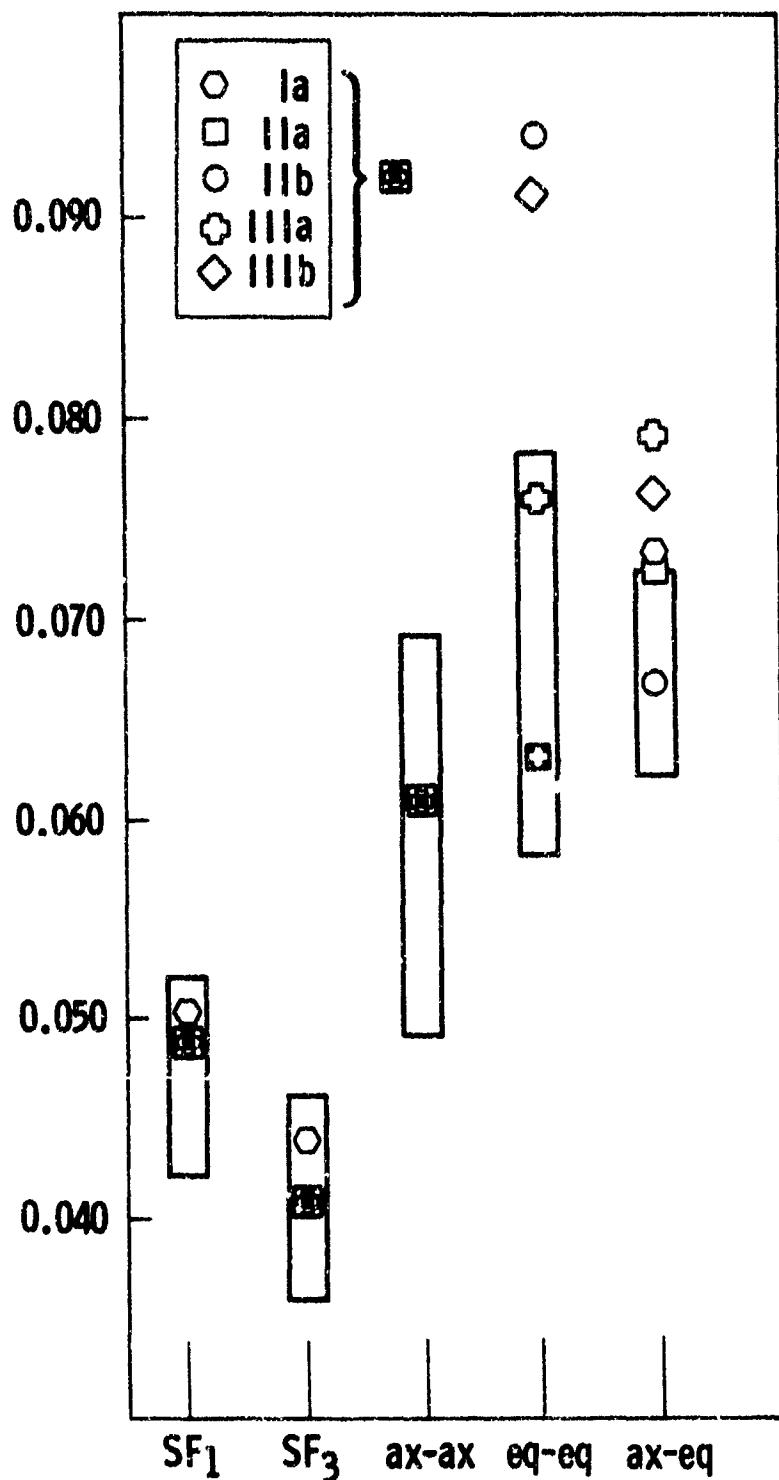
	$\langle q^2 \rangle_{\text{calc}}^{1/2}$					$\langle q^2 \rangle_{\text{obs}}^{1/2}$	
	Ia	IIa	IIa(MVFF)	IIb	IIIa	IIIb	
$\text{S-F}_1$ (ax)	0.050	0.049	0.050	0.049	0.049	0.049	$0.047 \pm 0.005$
$\text{S-F}_3$ (eq)	0.044	0.041	0.041	0.041	0.041	0.041	$0.041 \pm 0.005$
$\text{F}_1 \dots \text{F}_2$	0.061	0.061	0.061	0.061	0.061	0.061	$0.059 \pm 0.01$
$\text{F}_3 \dots \text{F}_4$	0.063	0.063	0.064	0.094	0.076	0.091	$0.068 \pm 0.01$
$\text{F}_1 \dots \text{F}_3$ ( $\nu_5 = 200 \text{cm}^{-1}$ )	0.091	0.091	0.091	0.086	0.096	0.094	$0.067 \pm 0.005$
( = 400 )	0.074	0.073	0.074	0.068	0.080	0.077	
( = 600 )	0.070	0.069	0.070	0.064	0.076	0.075	
( = 800 )	0.068	0.068	0.068	0.063	0.075	0.072	

Diagram Caption

Figure 1. Mean amplitudes of vibration ( $\text{\AA}$ ) of  $\text{SF}_4$  for bonded and nonbonded distances. Rectangles represent experimental electron diffraction values tested according to ref. 8. Crosses, squares, diamonds, and circles represent amplitudes computed for the different assignments.

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## Vibrational Spectrum and Force Constants of the $\text{SF}_5\text{O}^-$ Anion

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The  $\text{CsF}\text{-}\text{SF}_5\text{O}$  adduct has been prepared and characterized by infrared and Raman spectroscopy. All eleven fundamental vibrations expected for a pseudooctahedral anion of symmetry  $C_{4v}$  have been observed and are assigned. A modified valence force field has been computed for  $\text{SF}_5\text{O}^-$  and suggests an SO bond order of approximately 1.5.

### Introduction

The existence of a  $\text{CsF}\text{-}\text{SF}_4\text{O}$  adduct has been reported<sup>1</sup> in 1960 by Smith and Englehardt and in 1964 by Ruff and Lustig.<sup>2</sup> However, no details were given regarding its preparation or properties. In a subsequent paper Lustig and Ruff described<sup>3</sup> the synthesis of  $\text{Cs}^+\text{SF}_5\text{O}^-$  from  $\text{CsF}$  and  $\text{SF}_4\text{O}$  in  $\text{CH}_3\text{CN}$  solution. The ionic formulation of this adduct was substantiated<sup>3</sup> by its  $^{19}\text{F}$  nmr spectrum which showed a characteristic  $\text{AB}_4$  pattern. The vibrational spectrum of this interesting compound is essentially unknown, since only four infrared absorptions were published.<sup>3</sup> In this paper we wish to report the complete vibrational spectrum of the  $\text{SF}_5\text{O}^-$  anion and the results from a force constant computation.

### Experimental Section

**Materials and Apparatus.** Volatile materials used in this work were manipulated in a well-passivated (with  $\text{ClF}_3$ ) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm  $\pm$  0.1%). Sulfur oxide tetrafluoride was prepared by the method<sup>2</sup> of Ruff and Lustig from  $\text{SF}_4\text{O}$  and  $\text{F}_2$  and was purified by fractional condensation. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250  $\text{cm}^{-1}$  with an accuracy of  $\pm 2 \text{ cm}^{-1}$  for sharp bands. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the presssing operation.

The Raman spectra were recorded with an accuracy of  $\pm 2 \text{ cm}^{-1}$  using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to  $\sim -25^\circ$ , and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or melting point capillaries were used as sample containers. For the conical tubes the axial viewing-transverse excitation technique and for the capillaries the transverse viewing-transverse excitation techniques were used.

**Preparation of  $\text{CsSF}_5\text{O}$ .** A prepassivated (with  $\text{ClF}_3$ ) 30-ml 316 stainless steel cylinder was loaded with dry, powdered  $\text{CsF}$  (9.93 mmol). Purified  $\text{SF}_4\text{O}$  (16.1 mmol) was added to the cylinder at  $-196^\circ$ . After warming to ambient temperature overnight, the cylinder was heated at  $90^\circ$  for 5 days. Upon recooling to room temperature, all volatiles were removed *in vacuo* and trapped at

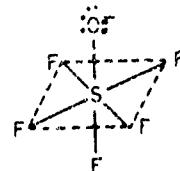
$-196^\circ$ . The recovered  $\text{SF}_4\text{O}$  (7.32 mmol) indicated that 88.5% of the  $\text{CsF}$  had been converted to  $\text{CsSF}_5\text{O}$ . Confirmation of this was obtained by pyrolyzing a sample of the complex at approximately  $250^\circ$  for 10 min while pumping the evolved gas through a trap cooled to  $-196^\circ$ . The evolved gas was identified as  $\text{SF}_4\text{O}$  and the amount found corresponded to an 82% conversion of  $\text{CsF}$  to  $\text{CsSF}_5\text{O}$ . A similar experiment exposing KF to  $\text{SF}_4\text{O}$  at temperatures up to  $125^\circ$  for several days did not result in any complexing.

### Results and Discussion

**Synthesis and Properties.** In the absence of a solvent, heating was required to achieve a significant conversion of  $\text{CsF}$  to  $\text{CsSF}_5\text{O}$ . The conversion obtained in the present study is comparable to that of 76% previously achieved<sup>3</sup> by the use of  $\text{CH}_3\text{CN}$  as a solvent. The reversibility of the formation reaction was demonstrated by the pyrolysis experiment which resulted in  $\text{SF}_4\text{O}$  as the only volatile product.  $\text{CsSF}_5\text{O}$  is a white, crystalline solid and does not show any detectable dissociation pressure at ambient temperature; attempts to synthesize the analogous potassium salt failed under similar reaction conditions. This is not surprising since the stability of salts of this type generally decreases with decreasing cation size.

**Vibrational Spectra.** Figures 1 and 2 show the Raman and the infrared spectra, respectively, of  $\text{CsSF}_5\text{O}$ . The absorption between 300 and 250  $\text{cm}^{-1}$  in the infrared spectrum is due to the AgBr window material. The observed frequencies are listed in Table I.

Analogy with isoelectronic  $\text{SF}_5\text{Cl}^{4,5}$  and the typical  $\text{AB}_4$   $^{19}\text{F}$  nmr pattern previously reported<sup>3</sup> for  $\text{SF}_5\text{O}^-$  suggests the following square-bipyramidal structure of symmetry  $C_{4v}$  for  $\text{SF}_5\text{O}^-$ :



For this ion of symmetry  $C_{4v}$ , 11 fundamentals are expected. These are classified as  $4 A_1 + 2 B_1 + B_2 + 4 E$ . All 11 modes should be Raman active, whereas only the  $A_1$  and  $E$  modes should be infrared active. The assignment of the observed bands to the individual modes is given in Table I and is supported by the following arguments. The very intense infrared band at  $1154 \text{ cm}^{-1}$  must be due to the SO stretching mode. As expected for an  $A_1$  mode it was also observed in the Raman spectrum. Its high frequency rules out any alternate assignment. Comparison with the cor-

\* Address correspondence to this author at Rocketdyne.  
(1) W. C. Smith and V. A. Englehardt, *J. Amer. Chem. Soc.*, **82**, 3838 (1960).  
(2) J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).  
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(4) L. H. Cross, H. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 945 (1960).  
(5) I. E. Griffiths, *Spectrochim. Acta, Part A*, **23**, 2145 (1967).

Table I. Vibrational Spectrum of  $\text{CsSF}_5\text{O}$  Compared to Those of  $\text{SF}_5\text{Cl}$  and  $\text{IF}_5\text{O}$ 

Obsd freq. $\text{cm}^{-1}$ , and intens				Assignment in point group				Approximate description of vibration
$\text{CsSF}_5\text{O}$		$\text{SF}_5\text{Cl}^a$		$\text{IF}_5\text{O}^b$		$\text{C}_{\text{v}}$		
IR	R	IR	R	IR	R	IR		
1154 vs	1153 (1)	402 s	403 (10) p	927 s	928 (4) p	$\text{A}_1$	$\nu_1$	$\nu(\text{XY})$
735 v-	722 (0.2)	855 vs	833 (0.2) p	680 s	680 (10) p	$\nu_2$	$\nu_2$	$\nu(\text{XF})$
697 m	697 (10)	707 s	704 (3.0) p	640 w	640 (9+) p	$\nu_3$	$\nu_{\text{sym}}(\text{XF}_4)$	
506 s	506 (1)	602 s	603 (0.2) p	360 s	c	$\nu_4$	$\delta_{\text{sym}}(\text{out-of-plane XF}_4)$	
	541 (3.3)		625 (0.7) dp		640 (9+) p	$\text{B}_1$	$\nu_{\text{sym}}(\text{out-of-phase XF}_4)$	
	472 (0.2)				(275) <sup>d</sup>	$\nu_5$	$\delta_{\text{asym}}(\text{out-of-plane XF}_4)$	
	452 (0.9)		305 (0.2) dp		305 (1) dp	$\text{B}_2$	$\nu_6$	$\delta_{\text{sym}}(\text{in-plane XF}_4)$
785 vc, br	780 (0.1) br	909 vs	927 (0.2) dp	710 vs	700 (0+) sh	$\nu_7$	$\nu_{\text{asym}}(\text{XF}_4)$	
606 s	607 (2.2)	287 vw	271 (0.6) dp	369 s	374 (1) dp	$\nu_8$	$\delta(\text{YXF}_4)$	
530 sh	530 (3)	379 mw	584 (0.1) dp	342 s	340 (4) dp	$\nu_9$	$\delta(\text{FXF}_4)$	
325 mw		441 m	442 (0.8) dp	e	205 (0+)	$\nu_{10}$	$\delta_{\text{asym}}(\text{in-plane XF}_4)$	

<sup>a</sup> L. V. Cross, M. L. Roberts, P. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 945 (1969). J. E. Griffiths, *Spectrochim. Acta, Part A*, **27**, 2145 (1967). K. O. Christe, C. J. Schack, and E. C. Curtis, *Inorg. Chem.*, **11**, 583 (1972). <sup>b</sup> D. F. Smith and G. M. Begun, *J. Chem. Phys.*, **55**, 2001 (1971). <sup>c</sup> Band masked by  $\nu_9$  and  $\nu_{10}$ . <sup>d</sup> Not observed, value estimated from combination band. <sup>e</sup> Below frequency range of spectrometer used.

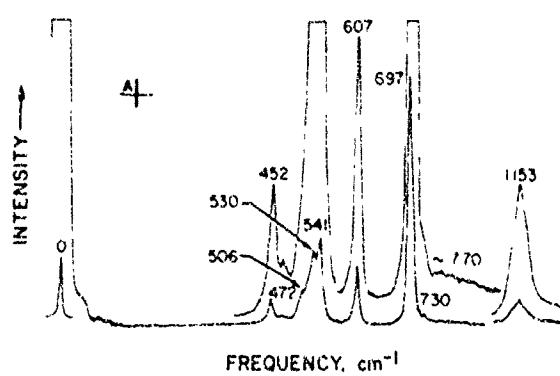


Figure 1. Raman spectrum of solid  $\text{Cs}^*\text{SF}_5\text{O}$ . A indicates spectral slit width.

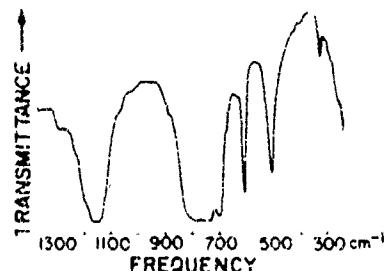


Figure 2. Infrared spectrum of solid  $\text{Cr}^*\text{SF}_5\text{O}^-$  as an AgBr disk.

responding mode in  $\text{SF}_5\text{O}^+$  ( $1538 \text{ cm}^{-1}$ )<sup>6</sup> and  $\text{SF}_5\text{O}$  ( $1380 \text{ cm}^{-1}$ )<sup>7</sup> shows the expected frequency decrease with an increasing formal negative charge. The  $\text{SF}_5\text{O}^-$  anion should have four additional stretching modes. Three of these belong to the approximately square-planar  $\text{SF}_4$  part and one involves the unique fluorine ligand. Of these, the totally symmetric  $\text{SF}_4$  stretching mode of species  $\text{A}_1$  should result in the most intense Raman line and is consequently assigned to the Raman band at  $697 \text{ cm}^{-1}$ . As expected for species  $\text{A}_1$ , this Raman band has an infrared counterpart. The antisymmetric  $\text{SF}_4$  and the SF stretching modes in  $\text{SF}_5\text{Cl}$  are both of very high intensity in the infrared and of very low intensity in the Raman spectrum<sup>4,5</sup> and occur at fre-

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quencies higher than that of  $\nu_{\text{sym}}(\text{SF}_4)$  ( $\text{A}_1$ ). Consequently, for  $\text{SF}_5\text{O}^-$  these two modes are assigned to the two weak Raman lines at  $780$  and  $722 \text{ cm}^{-1}$ , respectively. Of these two, the  $780\text{-cm}^{-1}$  line is attributed to  $\nu_{\text{asym}}(\text{SF}_4)$  owing to its width, lower Raman intensity, and larger frequency separation from  $\nu_{\text{sym}}(\text{SF}_4)$  ( $\text{A}_1$ ). Both Raman bands show as expected a very intense infrared counterpart. Owing to the broadness of  $\nu_{\text{asym}}(\text{SF}_4)$ , these two bands are poorly resolved in the infrared spectrum. The broadness of  $\nu_{\text{asym}}$  was also observed for several other approximately square-planar  $\text{XF}_4$  groups, such as  $\text{BrF}_4^-$ ,<sup>8</sup>  $\text{ClF}_4^-$ ,<sup>9</sup> or those in  $\text{SF}_5^-$  and  $\text{SeF}_5^-$ ,<sup>10</sup> and hence appears to be quite general. The remaining, yet unassigned, stretching mode,  $\nu_{\text{sym}}(\text{out-of-phase SF}_4)$  ( $\text{B}_1$ ), should be of medium Raman intensity, should ideally have no infrared counterpart, and should occur in the range  $500$ – $600 \text{ cm}^{-1}$ . Since both the  $506\text{-}$  and  $607\text{-cm}^{-1}$  Raman lines show very intense infrared counterparts, only the  $530$ - or the  $541\text{-cm}^{-1}$  line might belong to  $\nu_{\text{sym}}(\text{SF}_4)$  ( $\text{B}_1$ ). Based upon its higher Raman intensity and frequency, we prefer to assign  $541 \text{ cm}^{-1}$  to  $\nu_{\text{sym}}(\text{SF}_4)$  ( $\text{B}_1$ ).

There are six frequencies left for assignment to the six deformational modes. Of these, the O- $\text{SF}_4$  wagging mode (E) should have the highest frequency since it involves a motion of the oxygen atom, which has partial double-bond character (see below). Furthermore, this mode should result in a relatively intense band in both the infrared and Raman spectra. Consequently, this mode is ascribed to  $607 \text{ cm}^{-1}$ . By comparison with  $\text{SF}_5\text{Cl}$ ,<sup>4,5</sup>  $\text{SF}_5^-$ ,<sup>10</sup> and  $\text{SeF}_5\text{Cl}$ ,<sup>11</sup> one would expect  $\delta_{\text{asym}}(\text{in-plane SF}_4)$  (E) to have the lowest frequency of the  $\text{SF}_5$  group deformational modes and to be infrared active. Consequently, this mode is assigned to the  $325\text{-cm}^{-1}$  infrared band. Of the remaining two yet unassigned infrared-active deformational modes, the  $\delta_{\text{sym}}(\text{out-of-plane SF}_4)$  or umbrella mode ( $\text{A}_1$ ) should result in a very intense infrared band of relatively high frequency.<sup>4,5,10,11</sup> Consequently, this mode is assigned to  $506 \text{ cm}^{-1}$ , leaving  $530 \text{ cm}^{-1}$  for assignment to the F- $\text{SF}_4$  wagging mode (E). The two remaining, yet unassigned in-

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(10) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, *Inorg. Chem.*, **11**, 1679 (1972).

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Table II. Symmetry Force Constants of  $\text{SF}_3\text{O}^-$ 

$A_1$	$\nu_1$	1154	$F_{11} = f_D$	6.46
	$\nu_2$	733	$F_{22} = f_R$	3.75
	$\nu_3$	697	$F_{33} = f_r + 2f_{rr} + f_{rr}'$	5.43
	$\nu_4$	506	$F_{44} = 1/2(f_\beta + 2f_{\beta\beta} + f_{\beta\beta}') + f_\gamma + 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} - 4f_{\beta\gamma}' - 2f_{\beta\gamma}''$	2.52
			$F_{12} = f_{RD}$	0.66
$B_1$	$\nu_5$	541	$F_{55} = f_r - 2f_{rr} + f_{rr}'$	3.28
	$\nu_6$	472	$F_{66} = 1/2(f_\beta - 2f_{\beta\beta} + f_{\beta\beta}') + f_\gamma - 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} + 4f_{\beta\gamma}' - 2f_{\beta\gamma}''$	3.19
$B_2$	$\nu_7$	452	$F_{77} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}'$	1.46
$E$	$\nu_8$	785	$F_{88} = f_\gamma - f_{rr}'$	2.84
	$\nu_9$	607	$F_{99} = f_\gamma - f_{\gamma\gamma}'$	2.22
	$\nu_{10}$	530	$F_{1010} = f_\alpha - f_{\alpha\alpha}'$	2.62
	$\nu_{11}$	325	$F_{1111} = f_\beta - f_{\beta\beta}'$	1.21
			$F_{1111} = f_{\gamma\gamma} - f_{\gamma\gamma}'$	0.40
			$F_{1111} = \sqrt{2(f_{\alpha\alpha} - f_{\alpha\alpha}')}$	0.50
			$F_{1111} = f_{\beta\beta} - f_{\beta\beta}'$	0.28

<sup>a</sup> Stretching constants in mdyn/Å, deformation constants in mdyn/Å radian<sup>2</sup>, and stretch-bend interaction constants in mdyn/Å radian<sup>2</sup>. infrared inactive modes of species  $B_1$  and  $B_2$ , respectively, belong to the Raman lines at 472 and 452 cm<sup>-1</sup>. Since, for numerous structurally related species,  $\delta_{\text{asym}}$  (out-of-plane  $\text{SF}_4$ ) ( $B_1$ ) either has not been observed or was of very low intensity,<sup>8,9,12</sup> this mode is assigned to the very weak Raman line at 472 cm<sup>-1</sup>. Hence, the last yet unassigned Raman line at 452 cm<sup>-1</sup> should represent  $\delta_{\text{sym}}$  (in-plane  $\text{SF}_4$ ) ( $B_2$ ).

Comparison of the  $\text{SF}_3\text{O}^-$  assignment with that made for  $\text{SF}_3\text{Cl}^4,5$  (it should be noted that the assignment given in ref 7 for  $\nu_{11}$  (E) is likely to be incorrect<sup>11</sup>) shows satisfactory agreement (see Table I). The slight discrepancy in the relative Raman intensities observed for  $\nu_{10}$  (E) between the two species might be ascribed to increased coupling between  $\nu_9$  and  $\nu_{10}$  in  $\text{SF}_3\text{O}^-$  due to O being more similar in mass to F than Cl. This might result in a symmetric and antisymmetric rather than in a characteristic F-SF<sub>4</sub> and OSF<sub>4</sub> wagging motion. This assumption appears to be supported by the spectrum<sup>13</sup> of isoelectronic  $\text{IF}_3\text{O}$  (see Table I) for which the Raman intensity of  $\nu_{10}$  is higher than that of  $\nu_9$ .

Of the four infrared bands previously reported<sup>3</sup> for  $\text{CsSF}_3\text{O}$  only the two weaker ones agree with our observations. Furthermore, the previously suggested<sup>3</sup> assignment of the SO stretching mode to a broad band centered at 718 cm<sup>-1</sup> is obviously incorrect.

In summary, all 11 fundamentals of  $\text{SF}_3\text{O}^-$  have been observed and an assignment is offered. The observed vibrational spectrum definitely supports the proposed structural model of symmetry  $C_{4v}$ .

**Force Constants.** A normal-coordinate analysis was carried out to aid the spectral assignment. The kinetic and potential energy metrics were computed by a machine method,<sup>14</sup> assuming the following geometry and coordinate definitions.  $R_{\text{SF}} = r_{\text{SF}} = 1.60 \text{ \AA}$ ,  $D_{\text{SO}} = 1.47 \text{ \AA}$ ,  $\alpha(\text{SF}) = \beta(\text{F'SF}) = \gamma(\text{OSF}) = 90^\circ$ , where F' refers to the axial (unique) fluorine ligand. The symmetry coordinates used were identical with those reported<sup>13</sup> for  $\text{IF}_3\text{O}$ . The bond lengths were estimated by comparison with similar molecules using the correlation<sup>15</sup> noted by Gillespie and Robinson between stretching frequencies and bond lengths. The deformation coordinates were weighted by unit (1 Å) distance.

The force constants were calculated by trial and error with the aid of a time-sharing computer to get exact agreement between the observed and computed frequencies using the simplest possible modified valence force field. Unique

(12) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

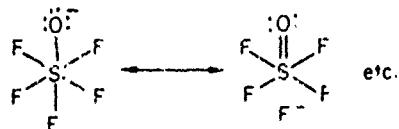
(13) D. F. Smith and G. M. Begun, *J. Chem. Phys.*, **43**, 2001 (1965).

(14) E. C. Curtis, *Spectrochim. Acta, Part A*, **27**, 1989 (1971).

(15) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963).

force constants could not be computed since the general valence field has 36 constants and there are only 11 observed frequencies. It was found, that for the  $A_1$  block the values of  $F_{11}$  and  $F_{22}$  were strongly influenced by the value of the interaction constant  $F_{12}$ . Since in isoelectronic  $\text{SF}_2\text{Cl}^{16}$  and in  $\text{IF}_3\text{O}^{13}$  the equatorial and axial fluorine atoms do not significantly differ in their stretching force constants and since in  $\text{SF}_3\text{O}^-$  the equatorial SF stretching force constant  $f_r$  is about 3.6 mdyn/Å, we prefer for  $\text{SF}_3\text{O}^-$  a force field with  $F_{22} = f_R \approx f_r$ . Surprisingly, the interaction constant  $F_{13} = 2f_{RD}$  had little influence on the frequencies of  $\nu_1$  and  $\nu_3$ . Hence, its value might be comparable to that of  $F_{12}$  although it is not required for obtaining a fit between the computed and observed frequencies. The computed symmetry force constants are listed in Table II. The interaction constants not listed were assumed to be zero.

The following values were obtained for the more important internal force constants:  $f_D = 6.46$ ,  $f_R = 3.75$ ,  $f_r = 3.60$ ,  $f_{RD} = 0.66$ ,  $f_{rr} = 0.54$ , and  $f_{rr}' = 0.75$  mdyn/Å. Significantly larger values of about 4.6 and 7.7 mdyn/Å are possible for  $f_R$  and  $f_D$ , respectively, by assuming a much smaller value for  $f_{RD}$ . However, the resulting large difference between  $f_R$  and  $f_r$  renders such a force field less likely. In spite of these uncertainties in the force constants, certain conclusions can be reached. The value of the SO stretching force constant  $f_D$  (6.5 mdyn/Å) is much lower than those of 10-12 mdyn/Å generally found for S=O double bonds.<sup>15,16</sup> Its value is comparable to that found for the  $\text{SO}_4^{2-}$  anion (7.44 mdyn/Å<sup>16</sup>) indicating for  $\text{SF}_3\text{O}^-$  a SO bond order of about 1.5. Furthermore, the values of the SF stretching force constants,  $f_R$  and  $f_r$ , are somewhat lower than those generally found for covalent SF bonds (4.5-6 mdyn/Å<sup>16</sup>) indicating significant ionic contributions to the SF bonds in  $\text{SF}_3\text{O}^-$ . These results are best interpreted in terms of the resonance structures



These structures together with orbital-following effects could also account for the unusually strong coupling between the SO and SF stretching modes suggested by the force constant computation.

**Registry No.**  $\text{CsF}\cdot\text{SF}_3\text{O}$ , 37862-11-6.

**Acknowledgment.** We are indebted to the Office of Naval Research, Power Branch, for financial support.

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## VIIBRATIONAL SPECTRA OF TRIFLUOROACETATES

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### Abstract

Infrared and Raman spectra of  $\text{CsI(O}_2\text{CCF}_3)_4$  and  $\text{Cs}_3\text{I(C}_2\text{CCF}_3)_6$  are reported and compared to those of the free trifluoroacetate anion and covalent trifluoroacetyl compounds. The bonding of the trifluoroacetate group in  $[\text{I(O}_2\text{CCF}_3)_4]^-$  is best interpreted as being covalent with strong ionic contributions. The vibrational spectrum of the free trifluoroacetate ion is reassigned.

### Introduction

The trifluoroacetate group is frequently used as a ligand in coordination chemistry. In most cases, vibrational spectroscopy is used to postulate either ionic, covalent, monodentate, or bidentate structures. However, these postulates are frequently based exclusively on minor frequency changes or splittings and consequently are not convincing. The recent synthesis [1] of  $\text{Cs}^+[\text{I(O}_2\text{CCF}_3)_4]^-$  presented an opportunity to study the vibrational spectrum of a trifluoroacetato ligand expected to be considerably more covalent than metal trifluoracetates, but more polar than

organic trifluoroacetyl compounds. The covalent character of the trifluoroacetato ligand in its iodine (III) compound is suggested by the nature of its analogous perchlorato [2] and nitrate [3] salts,  $\text{Cs}^+[\text{I}(\text{OCLO}_3)_4]^-$  and  $[\text{N}(\text{CH}_3)_4]^+[\text{I}(\text{NO}_3)_4]^-$ , respectively. In addition, the skeleton of  $\text{I}(\text{O}_2\text{CCF}_3)_4^-$  might be expected to have relatively high symmetry since the  $\text{IF}_4^-$  anion was recently shown [4] to be square planar. When comparing the assignments reported [5 - 8] for the free trifluoroacetate anion with those more recently reported [9 - 12] for a number of simple covalent trifluoroacetyl compounds, the need of revising the assignments for the free ion became obvious.

### Experimental

The preparation of  $\text{CsI}(\text{O}_2\text{CCF}_3)_4$  and  $\text{Cs}_3\text{I}(\text{O}_2\text{CCF}_3)_6$  has previously been described [1]. Silver trifluoroacetate was prepared from  $\text{Ag}_2\text{O}$  and  $\text{CF}_3\text{COOH}$  and vacuum dried at  $100^\circ\text{C}$  [7]. Sodium and cesium trifluoroacetate were purchased from Peninsular Chemical Research. The infrared spectra of the solids were recorded as dry powders in pressed  $\text{AgBr}$  disks on a Perkin Elmer Model 457 spectrophotometer in the range  $4000 - 280 \text{ cm}^{-1}$ . The instrument was calibrated by comparison with standard calibration points [13]. The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the  $4880 \text{ \AA}$  line of an Ar ion laser and melting point glass capillaries as sample containers in the transverse excitation-transverse viewing mode.

### Results and Discussion

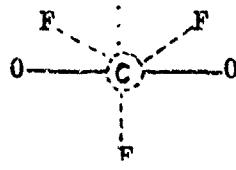
#### Observed Spectra

The vibrational spectra of solid  $\text{CsI}(\text{O}_2\text{CCF}_3)_4$ ,  $\text{Cs}_3\text{I}(\text{O}_2\text{CCF}_3)_6$ ,  $\text{NaO}_2\text{CCF}_3$ , and  $\text{AgO}_2\text{CCF}_3$ , and of an aqueous solution of  $\text{NaO}_2\text{CCF}_3$  are shown in Figures 1 and 2. The observed

frequencies are listed in Tables I and II. The Raman spectrum of an aqueous  $\text{AgO}_2\text{CCF}_3$  solution was also recorded. It closely resembled that of the sodium salt solution and, hence, is not listed. The spectra observed for the metal trifluoroacetates are in good agreement with those previously reported [5 - 8].

#### Assignments for the Trifluoroacetate Ion

A comparison between the assignments reported [5 - 8] for  $\text{CF}_3\text{CO}_2^-$  and those made for a series of trifluoroacetyl compounds [9] revealed major discrepancies. Consequently, the vibrational spectrum of the free trifluoroacetate ion was reassigned based on the results of the thorough studies of Berney [9] on trifluoroacetyl compounds. For the  $\text{CF}_3\text{CO}_2^-$  anion, a structure of symmetry  $C_s$  was assumed based on the known [14] structure of isoelectronic  $\text{CF}_3\text{NO}_2$ . This structure



has only one symmetry element, i.e., a symmetry plane perpendicular to the  $\text{CO}_2$  plane. Our revised assignments are summarized in Table I and were made by analogy with the well established assignments of  $\text{CF}_3\text{COF}$  [9]. The observed intensities and Raman polarization measurements are in good agreement with the predictions for symmetry  $C_s$ . For species a', one of the Raman bands ( $598 \text{ cm}^{-1}$ ) appears to be depolarized. However, the a' bands can be either polarized or depolarized, and the corresponding Raman band in  $\text{CF}_3\text{COF}$  alone showed a high depolarization ratio of 0.78 [9].

#### Nature of the Iodine-Trifluoroacetate Bond in $\text{CsI(O}_2\text{CCF}_3)_4$

Covalent or Ionic? The next and most difficult question deals with the nature of the trifluoroacetate ligand in  $\text{CsI(O}_2\text{CCF}_3)_4$ . A review of the literature on trifluoroacetate as a

ligand reveals numerous studies. However, the conclusions reached are often conflicting. This is due to the fact that most studies deal with trifluoroacetato complexes of metals. In this type of adduct, the trifluoroacetate ligand is essentially a free trifluoroacetate ion [15], which is only weakly bonded to the metal atom. As a consequence, the vibrational frequencies of the trifluoroacetato group are very similar to those of the free trifluoroacetate ion and exhibit only small relative changes. Without detailed structural data, such as x-ray diffraction studies, it is difficult to correlate these small frequency shifts with structural parameters. For example, small changes in the O-C-O bond angle due to the size of the metal atom or crystal packing are difficult to separate from effects caused by mono or bidentate coordination.

In  $\text{CsI}(\text{O}_2\text{CCF}_3)_4$ , the bands due to the  $\text{C}-\text{CF}_3$  part of the trifluoroacetate group are very characteristic and can readily be assigned (see Table II). Consequently, we will discuss mainly the vibrations associated with the  $\text{CO}_2$  group and the  $\text{IO}_4^-$  skeleton. To better understand the nature of the trifluoroacetate group, let us first consider the two extreme cases, i.e., the free trifluoroacetate anion and the highly covalent  $\text{CF}_3\text{C}(0)\text{OCH}_3$  molecule [11]. Whereas the average of the two CO stretching frequencies ( $1500 \text{ cm}^{-1}$  for  $\text{CF}_3\text{C}(0)\text{OCH}_3$  and  $1559 \text{ cm}^{-1}$  for  $\text{CF}_3(\text{CO}_2^-)$ ) and, hence, the average CO bond order changes little, their frequency separation ( $586 \text{ cm}^{-1}$  for  $\text{CF}_3\text{C}(0)\text{OCH}_3$  and  $242 \text{ cm}^{-1}$  for  $\text{CF}_3(\text{CO}_2^-)$ ) is very different. Furthermore, in the covalent trifluoroacetates of the type  $\text{XO}_2\text{CCF}_3$  bands due to the XO vibrations will appear and show increasing frequencies with increasing covalent character of the X-O bond. Inspection of the  $\text{CsI}(\text{O}_2\text{CCF}_3)_4$  spectrum reveals a CO stretching frequency separation of about  $386 \text{ cm}^{-1}$  and the presence of skeletal IO stretching modes as high as  $600 \text{ cm}^{-1}$ . Since the frequencies of the latter almost approach the frequency range expected for covalent I-O single bonds, the bonding

of the trifluoroacetate group in  $\text{Cs}(\text{O}_2\text{CCF}_3)_4$  is best described as being covalent with strong ionic contributions. The ionic nature of an  $\text{X}-\text{O}_2\text{CCF}_3$  bond might be expected to increase with decreasing electronegativity of the X atom. Experimental evidence for this trend has been found [16] for the trifluoroacetates of C, Si, Ge, and Sn. Within this series, the  $\text{C}=\text{O}$  stretching frequency decreases from  $1852 \text{ cm}^{-1}$  in  $\text{CF}_3\text{OC}(0)\text{CF}_3$  [16] to  $1750 \text{ cm}^{-1}$  in  $\text{Sn}(\text{O}_2\text{CCF}_3)_4$  [16], a frequency approaching those observed for  $\text{CsI}(\text{O}_2\text{CCF}_3)_4$  (see Table II). Further proof for the highly covalent nature of the trifluoroacetates of the group IV elements consists of their high volatilities [16]. Unfortunately, only the carbonyl stretching frequencies have been reported for these trifluoroacetates [16], except for  $(\text{CH}_3)_3\text{SnO}_2\text{CCF}_3$  which in  $\text{CCl}_4$  solution shows  $\text{C=O}$  stretching modes at 1720, 1660, and  $1400 \text{ cm}^{-1}$  [17]. The fact that a decrease of the carbonyl frequency is generally accompanied by an increase of the C-O frequency has also been recognized by Varetti and Aymonino [18].

Monodentate or Bidentate? The trifluoroacetate group could function as a monodentate or as a bidentate ligand. In connection with  $\text{Cs}(\text{O}_2\text{CCF}_3)_4$ , we will discuss mainly covalent ligands. Again, let us consider the two ideal cases, i.e., a monodentate and a symmetric bidentate trifluoroacetate group. A covalent monodentate group should exhibit a spectrum similar to that observed for  $\text{CH}_3\text{OC}(0)\text{CF}_3$  [11], i.e., a high  $\text{C}=\text{O}$  double bond and a low C-O stretching frequency. In addition, the trifluoroacetate group no longer possesses a symmetry plane. This removes the degeneracy between the  $\text{FCF}_2$  and the antisymmetric  $\text{CF}_3$  stretching mode and allows the observation of a total of three  $\text{CF}_3$  stretching modes in the  $1100 - 1300 \text{ cm}^{-1}$  frequency range. For a covalent symmetric bidentate, trifluoroacetate group, the two CO bonds should be equivalent, causing a strong mixing of their stretching motions. Instead of a  $\text{C}=\text{O}$  and a C-O stretch, one obtains a symmetric and an antisymmetric  $\text{CO}_2$  stretch with a CO bond order about 1.5. The

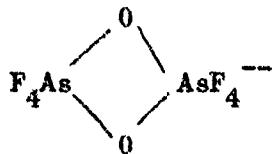
two  $\text{CO}_2$  stretching frequencies and their difference should be comparable to those of the free trifluoroacetate anion [19]. A minor decrease in the frequency difference might be expected for the bidentate ligand when compared to the free ion, if one assumes that the  $\text{XO}_2$  bonding in  $\text{X}^{\text{+}}\text{O}_2\text{C}^-$  will decrease the  $\text{CO}_2$  bond angle from the  $120^\circ$  value in the free ion towards  $90^\circ$ . This decrease in the bond angle would decrease the coupling between the two CO motions and make their frequencies more similar. In addition, one might expect the bidentate ligand to have the same symmetry ( $\text{C}_s$ ) as the free ion and, therefore, to show only two  $\text{CF}_3$  stretching modes owing to the degeneracy between  $\nu_3$  and  $\nu_{11}$  (see Table I). Consequently, distinction between a covalent symmetric bidentate ligand and the free ion may be difficult based upon the  $\text{CO}_2$  stretching frequencies alone. However, the appearance of the  $\text{XO}_2$  modes in the lower frequency range of the spectrum should clearly distinguish between the two possibilities.

Application of this reasoning to  $\text{CsI}(\text{O}_2\text{CCF}_3)_4$  clearly rules out the possibility of a symmetric bidentate structure. To what extent back donation of electrons of the carbonyl group (which is generally a good donor) to iodine in a monodentate structure, such as  $\text{I}(\text{O}_2\text{CCF}_3)_4^-$  takes place is difficult to judge from the presently available data and might be a matter of semantics.

#### Skeletal Modes

It was previously shown that the  $\text{IF}_4^-$  anion is square planar having symmetry  $\text{D}_{4\text{h}}$  [4]. For the  $\text{IO}_4$  skeleton in  $\text{I}(\text{O}_2\text{CCF}_3)_4^-$  such a planar configuration is unlikely.

Comparison with other oxygen bridged species such as  $\text{F}_5\text{AsOAsF}_5^{--}$  and



suggests X-O-X bond angles of about 140 and 95° [20] for mono - and bidentate bonding, respectively, of a trifluoroacetate group. The actual I-O-C bond angle should be influenced by the degree of back donation of electrons of the carbonyl oxygen to iodine and mutual repulsion between the atoms involved. In any case distortion of the  $\text{IO}_4^-$  part from symmetry  $D_{4h}$  is expected and a puckered arrangement of the oxygens around iodine is likely.

Comparison of the skeletal modes of  $\text{I}(\text{O}_2\text{CCF}_3)_4^-$  with those reported for the related  $\text{I}(\text{OCIO}_3)_4^-$  [2] and  $\text{I}(\text{OSO}_2\text{F})_4^-$  [21] anions shows relatively poor agreement. This indicates that the assumed structural models may be too simple and calls for structural studies such as x-ray diffraction, which will yield more accurate information. Similar data are required for  $\text{Cs}_3 \text{I}(\text{O}_2\text{CCF}_3)_6$ .

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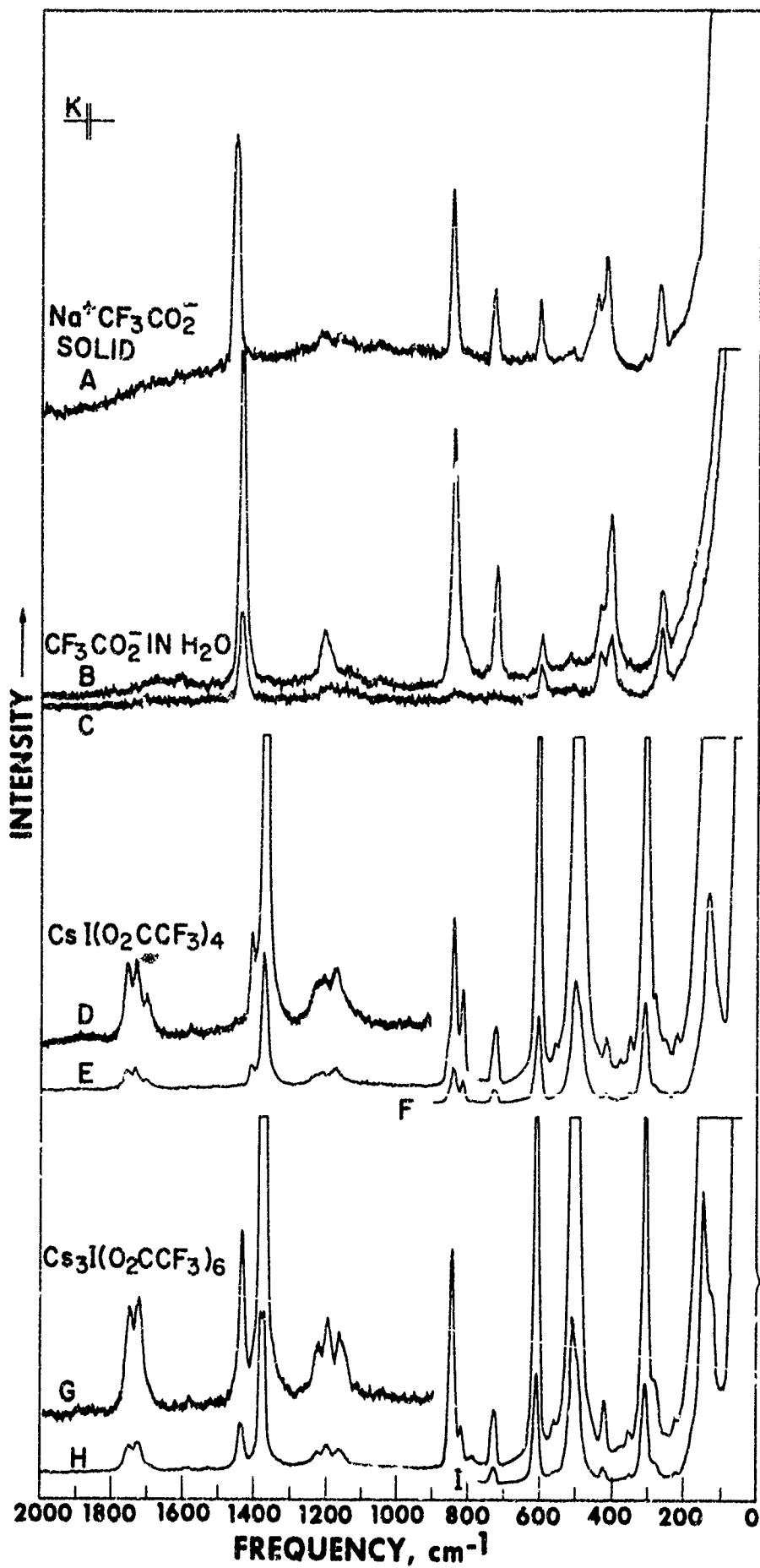
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DIAGRAM CAPTIONS

Figure 1. - Raman spectrum of solid  $\text{Na}^+\text{CF}_3\text{CO}_2^-$  (trace A), of an aqueous solution of  $\text{Na}^+\text{CF}_3\text{CO}_2^-$  (traces B and C, incident polarization perpendicular and parallel, respectively, of solid  $\text{CsI(O}_2\text{CCF}_3)_4$  at three different recorder voltages (traces D, E, and F), and of solid  $\text{Cs}_3\text{I(O}_2\text{CCF}_3)_6$  at three different recorder voltages (traces G, H, and I). K indicates spectral slit width; exciting line 4880 Å.

Figure 2. - Infrared spectrum of solid  $\text{Na}^+\text{CF}_3\text{CO}_2^-$  (trace A), of solid  $\text{Ag}^+\text{CF}_3\text{CO}_2^-$  (trace B), of solid  $\text{CsI(O}_2\text{CCF}_3)_4$  (trace C), and of solid  $\text{Cs}_3\text{I(O}_2\text{CCF}_3)_6$  (trace D) recorded as AgBr pellets.



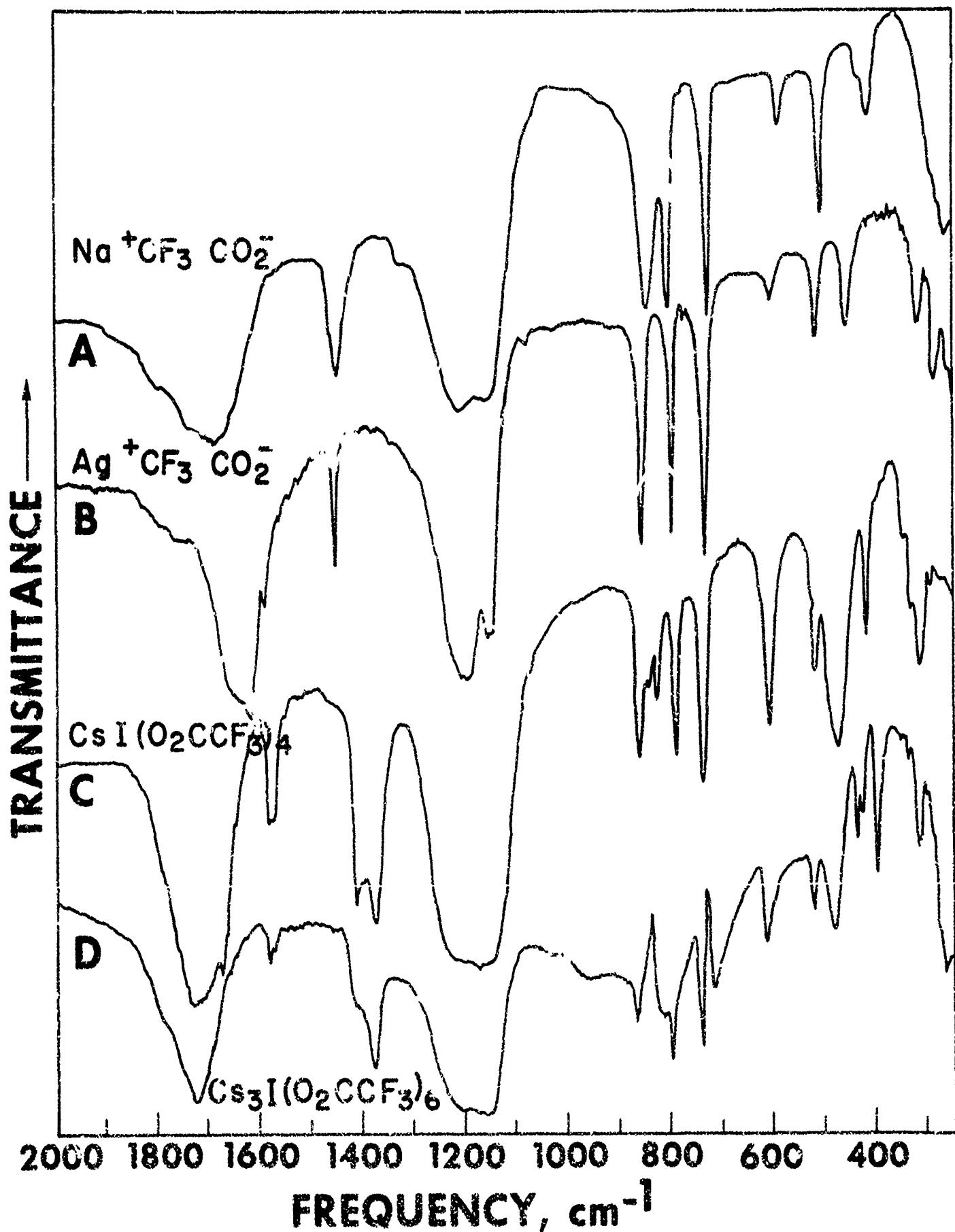


Figure 2

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Vibrational Spectra (cm<sup>-1</sup>) of the Triisobutyltin Ions and its Absorption in Point Group C<sub>3</sub> Compared to that of C<sub>2</sub> C<sub>3</sub>

Infrared Gas		Infrared Solid		Basic <sup>b</sup>		Infrared Solutes <sup>c</sup>		Basic <sup>b</sup>		Infrared Solid		Basic <sup>b,c</sup> Solid	
Infrared Gas	Basic Solid	Infrared Gas	Basic Solid	Infrared Gas	Basic <sup>b</sup>	Infrared Gas	Basic <sup>b</sup>	Infrared Gas	Basic <sup>b</sup>	Infrared Gas	Infrared Gas	Infrared Gas	Infrared Gas
$\text{CF}_3\text{C}\text{P}$		$\text{Na}^+\text{CF}_3\text{CO}_2^-$		$\text{Na}^+\text{CF}_3\text{CO}_2^-$		$\text{Na}^+\text{CF}_3\text{CO}_2^-$		$\text{Na}^+\text{CF}_3\text{CO}_2^-$		$\text{Na}^+\text{CF}_3\text{CO}_2^-$		$\text{Na}^+\text{CF}_3\text{CO}_2^-$	
1446 $\nu$	1443	1446 $\nu$	1434 (10)	1441 (10)	1433 vs, p	1438 (10) p	1450	1431 $\nu$	1449 (7)	$\nu'$	$\nu_1$	$\nu_{\text{sym CO}_2}$	
1340 $\nu$	1338	1313 $\nu$	1212 vs	1210 (0+) br	1211 (1.6)	1202 $\nu$ , p	1200 (1.1) p	1200 vs	1201 (1)	$\nu_2$	$\nu_{\text{sym CF}_3}$	$\nu_3$	
1364 $\nu$	1180 $\nu$				1188 (1.2)					$\nu_{\text{FCP}_2}$			
805 $\nu$	806 $\nu$	850 $\nu$	845, 841	847 vs	847 (7.2)	846 (3.2)	844 (6.0) p	845	852 $\nu$	849 (16)	$\nu_4$	$\nu_{\text{C-C}}$	
761 $\nu$	770,	807 $\nu$	804 vs				810 sh, p	803, 790	794 $\nu$		$\nu_5$	$\nu_{\text{bend CO}_2}$	
692 $\nu$	694 $\nu$	729 $\nu$	724	726 vs	725 (3)	728 (0.4)	721 $\nu$ , p	722	726 $\nu$		$\nu_6$	$\delta$ umbrella $\text{CF}_3$	
595 $\nu$	593 $\delta$	603	603 $\nu$	602 (2.7)	596 (1.2)	601 $\nu$ , p	598 (1.2) d $\nu$	600	606 $\nu$	$\nu_7$	$\nu_{\text{FCP}_2}$		
280 $\nu$	345 $\nu$			422 $\nu$	421 (4.8)	410 (1.6)	411 $\nu$ , p	409 (3.8) p	445	457 $\nu$	$\nu_8$	antigear rock <sup>d</sup>	
223 $\nu$	~224				—	224 (0.6)				$\nu_9$	gear rock <sup>d</sup>		
1699 $\nu$	1695	1688 vs, br		1676 (0+)	1683 $\nu$ , dp	1680 (0.3) br	1650, 1620	1640, 1615		$\nu_{10}$	$\nu_{\text{as CO}_2}$		
1214 $\nu$	~1360	1149 s	1143	1138 vs	1141 $\nu$	1145 (3)		1130	1130 $\nu$				
819 $\nu$	820 d $\nu$	616	516 $\nu$	516 (6+)	505 (9.8)	521 (6+)	520 (6+)	513	517 $\nu$		$\nu_{11}$	$\nu_{\text{as CF}_3}$	
423 $\nu$	427 d $\nu$		441 $\nu$	441 (2)	429 (1.2)	431 $\nu$ , dp	434 (1) d $\nu$	420	316 $\nu$		$\nu_{12}$	$\delta_{\text{as CF}_3}$	
363 $\nu$	246 d $\nu$	271 $\nu$		262 (1.2)	261 $\nu$ , dp	264 (1.9) d $\nu$	264	263 $\nu$	260 (1)		$\nu_{13}$	antigear wag <sup>d</sup>	
											$\nu_{14}$	gear wag <sup>d</sup>	
											$\nu_{15}$	$\tau$ C-C	

(a) For both  $\text{C}_2\text{CP}$  and  $\text{C}_2\text{CO}_2^-$ , symmetry  $C_2$  was assumed, but for  $\text{CP}\text{CP}$  (assuming free rotation of the  $\text{CP}_3$  group), the symmetry plane coincides with the  $\text{C}_2$  plane, whereas for  $\text{CP}_3\text{O}_2^-$  it is perpendicular to the  $\text{CO}_2$  plane.

(b) Discretized Raman intensities.

(c) The name is not listed.

(b) For description of this section, see Ref. 9.

TABLE II  
Vibrational Spectrum (cm<sup>-1</sup>) of Solid Cs<sup>+</sup> I(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>

<u>Infrared</u>	<u>Raman</u>	<u>Assignment</u>
1710 vs, br	1750 (0.3) 1725 (0.3) 1695 (0.1)	$\nu_{as} CO_2$ or $\nu_{C=O}$
1662 w		816 + 839 = 1655
1571 mw	1570 (0+)	
1561 mw		
1404 m	1405 (0.2)	$\nu_{sym} CO_2$ or $\nu_{C-O}$
1366 s	1369 (1.6)	
	1225 sh	$\nu_{sym} CF_3$
1140-1230 vs	1203 (0.2)	$\nu_{sym} FCF_2$
	1166 (0.2)	$\nu_{as} FCF_2$
854 mw	852 sh	
845 vw		
835 vw	839 (2.3)	$\nu_{C-C}$
820 w	816 (1.3)	
782 mw	781 (0+)	$\delta_{sciss} CO_2$
727 m	725 (0.7)	$\delta_{umbrella} CF_3$
602 m	604 (5.2)	$\delta FCF_2 + \nu_{sym}$ out of phase IO <sub>4</sub>
	555 (0.1)	
517 mw	520 sh	$\delta_{as} CF_3$
	501 (7.2)	$\nu_{sym}$ in phase IO <sub>4</sub>
490 sh	490 sh	
470 ms		$\nu_{as} IO_4$
416 mw	418 (0.3)	antigear rock
380 sh	378 (0.1)	
346 vw	346 (0.3)	
329 vw		
310 m		antigear wag ?
305 sh	306 (5.8)	$\delta IO_4$
293 vw		
275 sh	278 (0.1)	gear wag ?
	249 (0.2)	
	218 (0.3)	gear rock ?
	130 (10)	$\delta IO_4$